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**INNOVATIVE APPROACHES AND INSTRUMENTS IN MODELLING
AND MONITORING THE SHELF LIFE OF PACKAGED PERISHABLE
FOODS**

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Abstract

Shelf life models are mathematical equations that describe the relationship between food, package, and environment. Shelf life models are useful to predict the shelf life of food, to design food packages and to provide useful information. The accuracy by which these relationships are measured influences the reliability of the models. It is also necessary to know the relationships among the variables that play a significant role in defining food quality.

Many chemical, biological, and physical changes are dependent on moisture content or water activity in foods, whose changes may be dictated by the protection from the environment given by packaging in the distribution channel. Water activity is ruled by the moisture content in the food, which may change with time through the permeation process of water vapor across the packaging film. The equilibrium relationship between moisture content and water activity is explained by the sorption/desorption isotherm, which is obtained mostly by experiments determining moisture contents of the food samples equilibrated under different relative humidity conditions. Many attempts were conducted to express the equilibrium relationship by mathematical forms. The most widely used are the equations of Smith, Halsey, Henderson, Oswin, Inglesias, and Chirife. These equations are used in forecast models to determine the shelf life of moisture depending products. All these models assume that the relative moisture of the headspace of the packaging (which changes with the entrance of water vapour from the outside) is immediately in equilibrium with the product. This condition has not been verified experimentally and is based on theoretical considerations.

The aim of this PhD thesis is the study of innovative approaches and instruments to model and monitor the shelf life of packaged perishable foods. The crucial part of this work is to verify the theoretical assumption of immediate equilibrium assumed by moisture depending prediction models.

To achieve this result it has been developed and built an acquisition system based on moisture sensors, a recording unit and specific software to collect data. The system has been tested on different products and packages in order to define the proper materials and working conditions to define the experimental plan and the system settings.

A model system based on “Fetta biscottata” (a typical Italian bakery product chosen because of its regular shape, geometry, and uniformity among different batches) packaged in rigid EPS trays of different volumes has been chosen. This model system allowed to study how different quantities of product, different headspace volumes, and different packaging solutions influence the equilibrium between the relative humidity of the headspace and of the product and how this differences influence the shelf life prediction.

The model system studied in the present work has demonstrated that, in this case, the theoretical assumption generally used in the shelf life modelling, stating the immediate equilibrium between the headspace and the product relative moistures, is not verified. These relative moistures are not immediately in equilibrium but show an increasing difference correlated to the increase of the headspace volume/product weight ratio. This correlation has been studied and it has been described by a linear equation in the considered range.

The application of a shelf life prediction model to the studied system has shown that a correction is needed to avoid an underestimation of the shelf life. The application of this correction will be particularly interesting for the shelf life modelling of moisture depending products characterized by packaging solution with high headspace volumes.

In a second part of the work it has been studied the possibility to simplify the shelf life prediction for a category of products applying a unique shelf life model for all the products part of the category. The shelf life prediction is a labor and time intensive work, a simplification might be useful in real case studies, especially if the category includes high quantities of references.

The study on 14 different types of “Fetta biscottata” has demonstrated that it is possible to simplify the work only with simplifications based on a good knowledge of statistical indexes and their correct application.

Riassunto

I modelli di previsione della shelf life sono equazioni matematiche che descrivono il rapporto tra l'alimento, la confezione e l'ambiente. Essi sono utili strumenti per prevedere la shelf life degli alimenti ma anche per progettare gli imballaggi e fornire informazioni utili alla loro gestione. L'affidabilità dei modelli di previsione dipende molto dalla precisione con cui si misurano le relazioni tra alimento, confezione e ambiente, dall'approfondita conoscenza delle relazioni che intercorrono tra le variabili significative nel definire la qualità degli alimenti.

Le numerose modificazioni chimiche, fisiche e biologiche che possono avvenire durante la shelf life, dipendono in gran parte dal contenuto umido o di attività dell'acqua degli alimenti, le cui variazioni possono essere influenzate dalla protezione offerta dall'imballaggio durante la distribuzione commerciale. L'attività dell'acqua è governata dal contenuto umido del prodotto, che può modificarsi nel tempo attraverso il processo di permeazione del vapore acqueo attraverso l'imballaggio. Il rapporto di equilibrio tra il contenuto umido e l'attività dell'acqua è definito dall'isoterma di assorbimento/desorbimento, rilevata, per lo più, mediante esperimenti volti a determinare il contenuto umido dei campioni alimentari equilibrati a diverse condizioni di umidità relativa. Diverse equazioni matematiche sono state sviluppate negli anni per esprimere tale rapporto di equilibrio; le più usate sono le equazioni di Smith, Halsey, Henderson, Oswin, Iglesias e Chirife e vengono utilizzate nei modelli di previsione per determinare la shelf life dei prodotti alimentari sensibili agli scambi di umidità. Tutti questi modelli presuppongono che l'umidità relativa dello spazio di testa della confezione (che si modifica con l'ingresso di vapore acqueo dall'esterno) sia immediatamente in equilibrio con l'umidità relativa del prodotto. Questa assunzione non è stata finora verificata sperimentalmente e si basa su considerazioni teoriche.

Scopo di questa tesi di dottorato è lo studio di approcci e strumenti innovativi nella modellazione e nel controllo della shelf life di prodotti confezionati la cui deperibilità è prevalentemente umidità dipendente. Parte fondamentale di questo lavoro è stata la verifica dell'assunto teorico di immediato equilibrio alla base dei modelli di previsione della shelf life per prodotti sensibili agli scambi di umidità.

Per raggiungere questo obiettivo è stato progettato, costruito e sviluppato un sistema di acquisizione dati basato su sensori di umidità, dotato di una unità di registrazione e di uno specifico software. Il sistema è stato preliminarmente utilizzato con diversi prodotti e differenti soluzioni di confezionamento in modo da selezionare il prodotto e la confezione più appropriati e definire le migliori soluzioni per il piano sperimentale, le condizioni di lavoro e la strumentazione da utilizzare.

Il sistema modello scelto è basato su fette biscottate (un tipico prodotto da forno italiano adatto al presente lavoro a causa della sua forma regolare, la geometria e l'uniformità tra lotti diversi) confezionate in vaschette rigide di EPS di due differenti volumi. Il sistema modello ha permesso di studiare come diverse quantità di prodotto, diversi spazi di testa e diverse soluzioni di confezionamento influenzino l'equilibrio tra l'umidità relativa dello spazio di testa del prodotto e quella del prodotto e come questa differenza influenzi la previsione della shelf life.

Il presente lavoro ha dimostrato, tramite i dati forniti dal modello studiato, che l'assunto teorico in genere utilizzato nel modello di previsione della shelf life per prodotti umidità dipendenti, non è verificato. Infatti l'umidità relativa dello spazio di testa e l'umidità relativa del prodotto non sono immediatamente in equilibrio, bensì mostrano una differenza che aumenta all'aumentare del rapporto tra volume dello spazio di testa e peso del prodotto. Questa correlazione è stata analizzata ed è stata descritta da un'equazione lineare nell'intervallo considerato.

L'applicazione di un modello di previsione della shelf life al sistema modello in esame ha mostrato la necessità di una correzione per evitare una sottostima della shelf life del prodotto. L'applicazione di tale correzione può essere particolarmente interessante per la previsione della shelf life di prodotti sensibili agli scambi di umidità caratterizzati da soluzioni di imballaggio con elevato volume di spazio di testa.

Una seconda parte del lavoro ha studiato la possibilità di semplificare la previsione della shelf life per una intera categoria di prodotti, applicando un unico modello di previsione a tutti i prodotti appartenenti alla categoria. Questo tipo di previsione richiederebbe dispendio di lavoro e di tempo e una semplificazione potrebbe essere utile in applicazioni reali, in particolare per categorie di prodotti caratterizzate da elevate quantità di referenze.

Lo studio applicato a 14 diverse tipologie di fette biscottate ha dimostrato che è possibile semplificare il lavoro solo applicando formule basate su una valida conoscenza degli indici statistici tipici di questi modelli e sulla loro corretta applicazione.

1. Introduction

In the food products the expiration of shelf life is frequently caused by some deterioration leading to unacceptable quality and safety issues. The three main categories of food spoilage that can occur are physical spoilage, chemical spoilage, and microbiological spoilage. There are some overlaps among the three categories, and often spoilage in one category can help to promote spoilage in another one. There are several main factors that influence most types of spoilage. These factors include temperature, pH, water activity, exposure to oxygen and light, and nutrients or chemicals available in the food product (Singh & Anderson, 2004).

A food product, especially if it contains multiple ingredients, may have many deterioration modes, but it is not necessary to deal with all possible deterioration modes. Instead, efforts should be made to identify one or two major deterioration modes which occur most rapidly, because the product shelf life is limited by those fast deterioration modes, not by the slow ones. In some situations, two different deterioration modes may be related. The deterioration modes of a food product may be identified using a sensory panel or based on prior knowledge of the food product.

Food deterioration modes can be product dependent or package dependent. Product dependent deteriorations are food deteriorations driven by intrinsic stability of the food product, given by food formulation and processing conditions, not by environmental factors or packaging. Package dependent deteriorations are food deteriorations driven by environmental factors that are controllable by the packaging technologies. Those environment factors include oxygen, moisture, microbes and light from the ambient environment, against which the food product may be protected by using the package as a barrier to separate the product from the external environment.

When the major deteriorations modes are known, it is necessary to identify quality indexes to quantify and describe the deterioration. These quality indexes need to be measurable, reproducible, and relevant. Quality indexes may be subjective or objective. Subjective indexes have the advantage of being most relevant to the consumer acceptability, but they have the disadvantage that measurements have relatively low degree of reproducibility and are labor intensive to obtain. Objective quality indexes, instead, have the advantage that measurements have good reproducibility, but also have the disadvantage that the acquired data may not correlate well to consumer acceptability. In most cases, a combination of subjective and objective quality indexes is the best for describing the quality of a food product. To define shelf life properly, it is also necessary to define a critical limit for each quality index, below which the food product is no longer acceptable (Lee et al., 2008).

1.1 Food products degradation factors

All food products are subjected to a deterioration of quality due to a series of chemical phenomena, physical and biological processes involved in their conservation. These negative quality changes are induced by a primary event. The effects of the primary event deterioration induce a measurable change of a quality attribute of the product (Piergiovanni, 2002).

The primary events of the degradation can be divided into intrinsic and extrinsic events. In the first category all the components that participate to the degradative reactions are present in the formulation of the product. Therefore the degradation phenomena can be influenced directly only by modifying the composition of the food or by changing the production technology.

The category of extrinsic events is composed by degradation phenomena that are not caused by the surrounding environment. They are (Spiegel, 1992):

- light transmission;
- gas transmission;
- heat transmission;
- moisture transmission;

- mechanical stress.

1.1.1 Light transmission

Sunlight and artificial light can both act as a catalytic for various chemical reactions that can affect the quality of food.

Some electromagnetic radiation of light, for example, catalyzes the oxidation of fat favoring rancidity of foods that contain lipids. Many natural substances, such as pigments, have the ability to absorb incident light leading to undesired modifications.

Many vitamins are photodegradable (vitamin A, vitamin B2) and the products of these degradations are very reactive substances that interact with other constituents of the original product. Therefore in many cases the packaging has the function of acting as a selective filter and to protect from the electromagnetic radiation, absorbing the dangerous ones and letting through the innocuous ones (Cladman et al., 1998).

1.1.2 Gas transmission

There are many gaseous substances that can be transmitted to food or are released into the environment by themselves: oxygen, carbon dioxide (produced by fermentation or addition), volatile substances (organic vapors mainly) responsible for both positive and negative flavor characteristics.

The modification of the aromatic component of a food does not affect its biological and physical characteristics, however it causes a decrease of its sensorial characteristics.

Instead, oxygen is absorbed by food leading to oxidative reactions that cause modifications in color and flavor of the food. Also, if the food contains fat, oxygen leads to rancidity reactions that cause the characteristic unpleasant taste (Masi, 1996).

1.1.3 Heat transmission

Almost all chemical, biological and physical phenomena are accelerated by an increase in temperature, unless such increase does not involve any change in the structure concerned (denaturation, inactivation, cell death).

Enzymatic, and many of chemical reactions, increase significantly their speed even with a low increase in temperature. This increase is described by the Arrhenius equation:

$$k = k_0 * e^{\frac{-E_a}{RT}} \quad (1.1)$$

Where:

- k: reaction rate constant;
- k_0 : pre-exponential constant;
- E_a : activation energy $\left[\frac{J}{mol} \right]$;

- R: universal gas constant $\left[8.314 \frac{J}{K * mol}\right]$;
- T: absolute temperature $[K]$.

The value of activation energy E_a measures the sensitivity of the degradation reaction to temperature. It is a value that depends on factors such as water activity, moisture content, solids concentration and pH.

When the heat content changes often there is also an associated physical change that can be very important for quality, such as crystallization, solutions of solutes and phase changes.

1.1.4 Moisture transmission

The moisture content and water availability in food play a fundamental role in the stability and shelf-life of the product.

Many different phenomena depend on the moisture content of a food. They can be accelerated by the transfer of water between product and environment.

They can be (Saguy & Karel, 1980):

- microbiological events: every organism has a threshold of minimum relative humidity to grow;
- physical events that affect mainly the structure and consistency of the product: the crystallization of sugar, swelling of colloidal systems, modifications of crystallizable materials;
- chemical events: most of the chemical and enzymatic reactions are influenced by water through different mechanisms, sometimes very complex. In fact water is a solvent in the hydrolytic reactions; it is a product of condensation reactions and can lead to an agent that modifies the catalytic activity and other inhibitory substances.

It has also to be considered that the relative humidity is not constant but changes as a function of temperature.

1.1.5 Mechanical stress

From the production to the consumption a food product may be subjected to different mechanical stresses intentionally or accidentally. This can happen during packaging, warehouse storage, and transportation, placement on the shelves, the purchase phase, and the arrangement in the house. Shock and vibration can cause the loss of the food integrity. As in the case of loss of flavor, even the loss of integrity does not always affect the intrinsic quality of a food, not interfering with the sensory aspects, nutritional and toxicological. However, it can be extremely negative from a commercial point of view for the image of the product.

1.2 Relative humidity and adsorption isotherm

All chemical, physical and biological processes that involve the exchange of moisture between the food and the environment depend on the water availability not on the overall moisture content. The water availability can be expressed as partial vapor pressure, which is the ratio between the vapor

pressure of water contained in the product (p) and the vapor pressure of pure water at the same temperature (p_0).

This ratio is defined water activity (a_w) or equilibrium relative humidity, when expressed as a percentage:

$$a_w = \frac{p}{p_0} \quad (1.2)$$

$$\%RH = \frac{p}{p_0} * 100 \quad (1.3)$$

The vapor pressure, which is the pressure exerted by water molecules of the product that are released in the vapor phase, is a parameter strictly dependent on temperature. This parameter informs about the affinity of water molecules with the constituents of the product. The higher the affinity is and the lower the vapor pressure is, because a low amount of water molecules are released (Peri, 1996).

In the heterogeneous systems, as food can be considered, the reactivity of each molecular species is strongly correlated to the affinity with water molecules and to the competitiveness with the hydrophilic and hydrophobic sites.

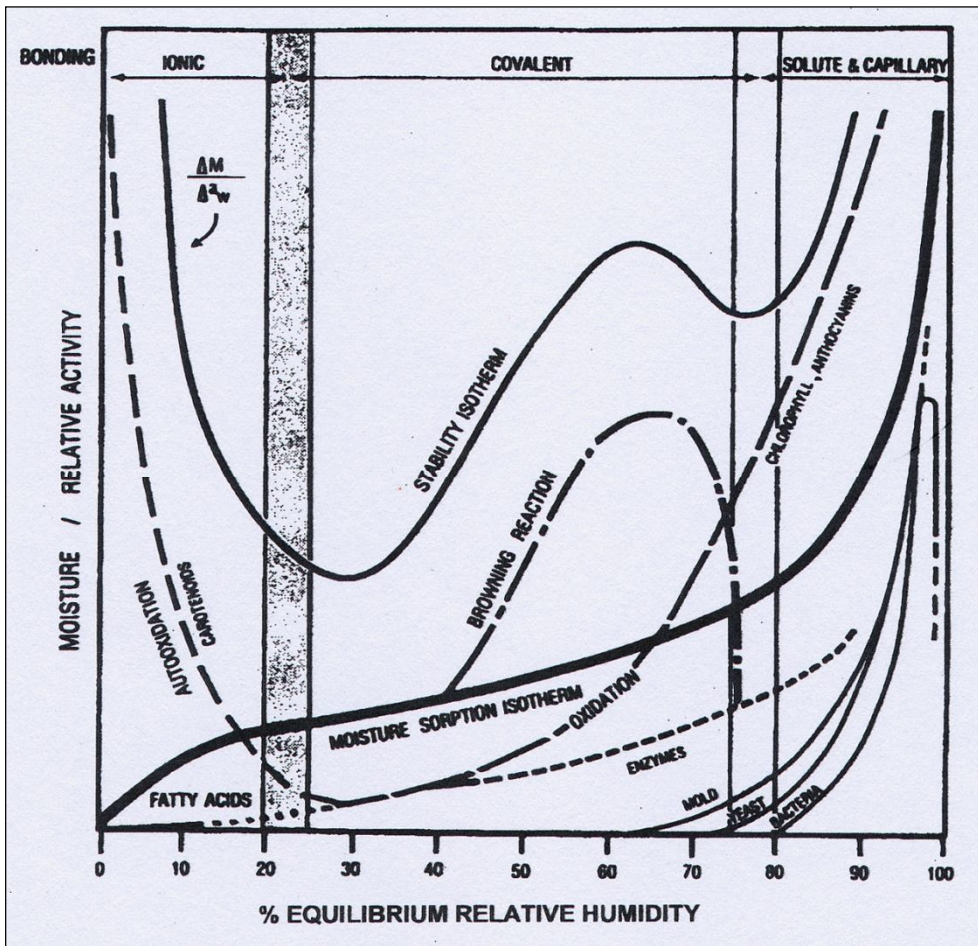
Small temperature changes or other factors that indirectly affect the water activity (light, additives, pH, and pressure) can induce changes in the molecular arrangement of water, which are reflected in the food quality and stability (Rockland & Nishi, 1980).

For this reason it is important to know what the water availability of a product is. The relationship between relative humidity at the equilibrium and the total moisture content (expressed as the amount of water for mass unit of dry product) is expressed in a graph called adsorption or desorption isotherm according to whether it is experimentally built by gradually hydrating or dehydrating the food.

The isotherm describes the behavior of the product during the equilibrium process with the environment humidity, adsorbing or desorbing water, according to its initial state.

Each food has a typical and specific isotherm. It is interesting to note that all the isotherms can be divided into three characteristic areas (figure 1.1) according to the water bonds.

Figure 1.1: adsorption isotherm.



The first area includes the lower equilibrium relative humidity values (0-25%). At these values the water is strongly linked to the preferential adsorption sites through hydrogen bonding and ionic interactions. The vapor pressure is low and the water has a high energy of adsorption.

The second area includes intermediate equilibrium relative humidity values, between 20 and 65%. The water is linked to the different components mainly with covalent bonds and the individual molecules are oriented in layers.

The third area includes the highest relative humidity values, from 75 to 100%. Water molecules are not chemically or physically linked to the product but are free and arranged disorderly. In this area the water is free to condense and the decrease of the vapor pressure is due to the capillary forces that are generated in the microstructure of the food (Peri, 1996; Rockland & Nishi, 1980).

In Figure 1.1, besides the adsorption isotherm of the product, are reported some other curves. They represent the main degradation reactions that can occur in food as a function of relative humidity equilibrium that can affect the food quality and stability.

1.3 Food packaging

Food packaging is a coordinated system designed for the efficient delivery of high quality, safe food products throughout every phase of the supply chain, from raw material production to food manufacture, packaging, retail, wholesale, consumer use, disposal, and recycling or other means of resource recovery.

A food package must serve one or more functions to justify its existence. Food packaging has four basic functions: protection, convenience, communication, and containment. A package design may be evaluated based on how well the package performs the required functions in a cost effective manner (Lee et al., 2008).

1.3.1 Protection

Protecting the food from physical damage, physiochemical deterioration, microbial spoilage, and product tampering is probably the most important function of packaging. Without proper protection, the food may become unappetizing, less nutritious, and unsafe to consume.

The required packaging protection depends on the stability and fragility of the food, the desired shelf life of the food package, and the distribution environment. Good package integrity is also required to protect against loss of hermetic condition and microbial penetration.

Generally, the protection function of packaging is limited to foods whose shelf lives are controlled by environmental factors relating to physical damage, humidity, oxygen, light, and, to some extent, temperature. Packaging is usually not effective for protecting foods whose shelf lives are controlled by internal factors (Lee et al., 2008).

1.3.2 Convenience

Convenience is an important function to satisfy the busy consumer lifestyle. Examples of convenient food packages are ready-to-eat meals, heat-and-eat meals, and self-heating packages. Examples of convenient features are easy opening, resealability, and microwavability. Innovations are constantly sought to provide more convenience without sacrificing quality or increasing costs (Lee et al., 2008).

1.3.4 Communication

The function of communicating is important to create brand identity and influence consumer buying decisions. The package communicates with the consumer through written texts, brand logo, and graphics. In many countries, nutritional facts such as calories, fat, cholesterol, and carbohydrate are required on all food packages.

The communication function is also important for facilitating distribution and retail checkouts. The barcode has virtually become an integral part of every commercial food package. Besides the barcode, there are other package devices, such as time-temperature indicator and radio frequency identification (RFID), which enable the package to communicate more effectively for the purpose of ensuring food quality and safety (Lee et al., 2008).

1.3.5 Containment

Containing the food product is the most basic function of packaging. The requirement for containment depends on the size, weight, form, and shape of the enclosed food; for example, a solid

food has different requirements from a liquid food. The containment function is also closely related to the rigidity of the package (Lee et al., 2008).

It is evident that there is not an ideal packaging solution for everything, for each product the most appropriate materials and the most appropriate construction techniques must be selected. In particular, for products with low moisture content, almost all the structural changes that have been described previously depend on the water content of the product. Its quantity, its availability and mobility in the product matrix influence the speed and the direction of moisture exchange between the product and the surrounding environment.

In these conditions the moisture exchange between the product and the surrounding environment has to be limited by a vapour barrier.

1.4 Permeability of food packaging polymers

The transport of gas or vapor through a food package can greatly influence the keeping quality of the packed food. Water vapor infiltrating the package can cause moisture gain leading to sogginess or microbial growth in food, while water vapor escaping from the package can cause moisture loss leading to undesirable textural changes in food.

On the contrary, there are occasions when the transport of gases and vapors is desirable. In modified atmosphere packaging of fresh produce, the exchange of oxygen, carbon dioxide, and water vapor through the package is necessary to accommodate the respiration and transpiration of the still bioactive product and to maintain an optimum gas composition in the package.

There is a subtle difference between gas and vapor, although these two terms are frequently used interchangeably. A gas refers to low-boiling-point molecules that are non condensable and exist only in the gaseous state at ambient temperature and atmospheric pressure. 'Permanent gases' describe oxygen, nitrogen, hydrogen, carbon dioxide, and other gases that follow the ideal behavior; for example, they obey Henry's Law and their permeabilities and diffusivities are constant, not concentration dependent. On the other hand, a vapor is condensable at ambient temperature. Condensation of water vapor may cause the problems of fogging on package surface and microbial growth on food surface. Water vapor and organic vapors often deviate from the ideal behavior, and their permeabilities and diffusivities are concentration dependent.

There are two major mechanisms by which gas or vapor may be transported through the package: permeation and leak. Permeation involves the exchange of a gas or vapor (also known as permeant) through a plastic film or package wall. Leak involves the exchange of gas or vapor through pinholes or channel leaks. Leaks from defective packages are often more influential than permeation in determining the overall transmission rate (Chung et al., 2003).

In the following paragraphs the three major steps (adsorption, diffusion, desorption) involved in the permeation process are described and a permeation equation based on this understanding is derived. To characterize the barrier properties of polymeric packaging materials, we introduce the term permeability (also known as permeability coefficient), defined as a product of diffusion coefficient and solubility coefficient (Lee et al., 2008).

1.4.1 Basic concepts of permeation

Permeation and gas barrier are closely related terms. Permeation is inversely proportional to gas barrier. A package which allows gas to permeate quickly is a package of low gas barrier. To protect foods that are oxygen or moisture sensitive, high gas barrier packages should be used to retard the rate of permeation.

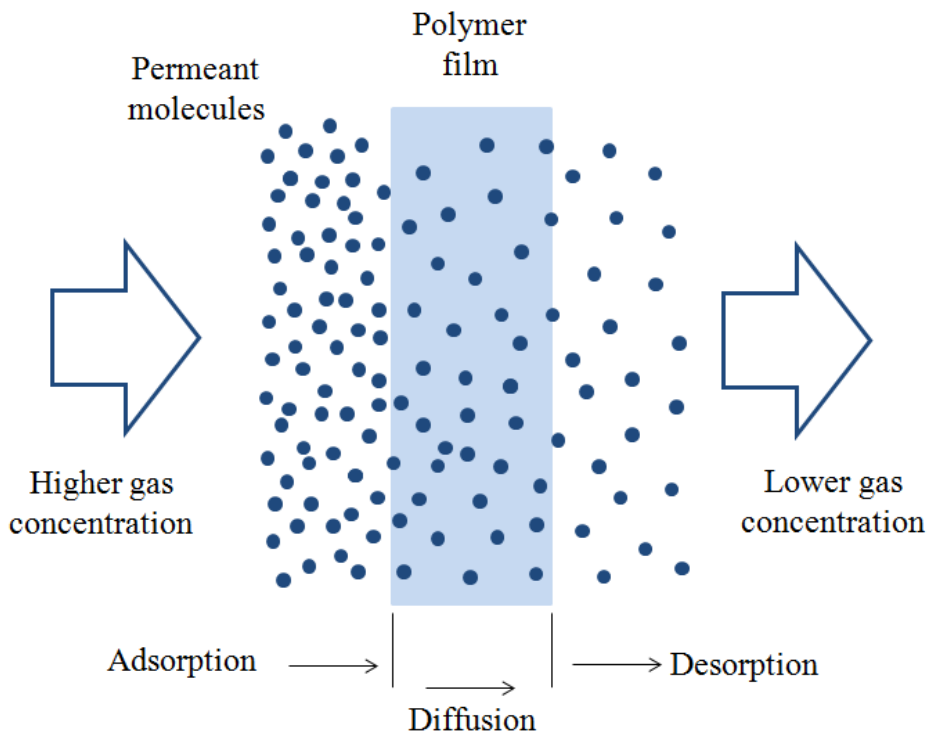
All packaging polymers are permeable to gas and vapor to various degrees. These polymers provide a wide range of permeability for different applications. Hence the study of permeation is important

to ensure that adequate gas barrier protection is provided for plastic pouches, plastic containers, and other plastic packages (Lee et al., 2008).

1.4.2 Mechanism of gas transport through permeation

Figure 1.2 shows that permeation of a permeant through a polymer film (or a package wall) is driven by concentration gradient in the direction from high to low concentration. The mechanism of permeation consists of three sequential steps: adsorption of the permeant onto the high concentration side of the film surface, diffusion of the permeant across the film, and desorption of the permeant from the low concentration side of the film surface.

Figure 1.2: permeation through a polymer film.



When measuring permeation rates, experiments are usually set up such that both sides of the film are exposed to the gas phase. In this case, the permeation process involves only the gas and solid phases, where the permeant in one gas phase (left side) enters the solid phase of the polymer film (middle) and exits to another gas phase (right side) (Lee et al., 2008).

1.4.3 Diffusion of permeant

Diffusion is the movement of molecules from a region of high concentration to a region of low concentration as a result of intermingling of the molecules due to random thermal agitation. While individual molecules move randomly with no sense of direction, the intermingling of the molecules

results in a net movement from high to low concentration. This means more molecules moving from a region of high concentration than those moving from the opposite direction. The diffusion of a permeant through a polymer film may be described by Fick's first law:

$$J = -D \frac{dc}{dx} \quad (1.4)$$

Where:

- J: diffusion flux $\left[\frac{\text{mol}}{\text{cm}^2 \text{ s}} \right]$;
- D: diffusion coefficient (also called diffusivity) $\left[\frac{\text{cm}^2}{\text{s}} \right]$;
- c: permeant concentration $\left[\frac{\text{mol}}{\text{cm}^3} \right]$;
- x: distance in the flow direction $[\text{cm}]$.

Since the increase in concentration is customarily associated with the positive x direction, a negative sign is needed in equation 1.4 to denote that diffusion is in the negative x direction or toward a lower concentration.

Diffusion flux J is the amount of permeant diffusing per area per time through a plane perpendicular to the flow direction. The term dc/dx is frequently referred to as concentration gradient or driving force of diffusion. When $dc/dx = 0$, net diffusion ceases. It does not mean the molecules are no longer moving, but that the rates of molecular movement on both sides of the film counterbalance each other. Diffusion coefficient D is a measure of the mobility of permeant molecules in the polymer film.

There are two types of behavior for molecular diffusion in polymer. Fickian behavior is characterized by concentration independent diffusion coefficients. This behavior is commonly observed for diffusion of permanent gases in polymers; for example, the diffusion coefficient of oxygen in a polyethylene (PE) film remains the same when oxygen concentration is changed from 21% to 100%. On the other hand, non-Fickian behavior is characterized by concentration dependent diffusion coefficients. This behavior is commonly observed for diffusion of water vapor or organic vapors in polar polymers such as nylon and EVOH, where strong interactions between the permeant and the polymer matrix exist (Lee et al., 2008).

1.4.4 Adsorption and desorption of permeant

Adsorption and desorption are related to the solution or sorption behavior of the permeant molecules in the polymer film, which is governed by the relative strengths of interactions between permeant/permeant, permeant/polymer, polymer/polymer.

The simplest or 'ideal' sorption isotherm is expressed by Henry's law:

$$c_s = Sp \quad (1.5)$$

Where:

- c_s : permeant concentration at the solid phase film surface $\left[\frac{\text{mol}}{\text{cm}^3} \right]$;
- p : partial pressure of permeant $[\text{atm}]$;
- S : solubility coefficient $\left[\frac{\text{mol}}{\text{cm}^3 \text{atm}} \right]$.

If the solubility coefficient S is concentration independent, then equation 1.5 expresses a linear relationship. This ideal behavior is applicable to the adsorption and desorption of permanent gases at atmospheric pressure, where the permeant/permeant and permeant/polymer interactions are weak compared to the polymer/polymer interactions.

Henry's Law provides a convenient means for estimating c_s once p and S are known. It is difficult to measure the permeant concentration at the film surface (c_s), but it is relatively easy to measure the permeant partial pressure (p) using a gas chromatograph or a portable gas analyzer (Lee et al., 2008).

1.4.5 Permeation rate

The individual steps of adsorption, diffusion, and desorption in the permeation mechanism may be integrated using the principle of mass balance because permeation involves the transport of mass (i.e., permeant molecules) from one place to another. By applying the mass balance, along with Fick's First Law and Henry's Law, useful equations may be obtained to guide the design of food packages.

A useful equation to describe the permeation rate at steady state (no permeant accumulation in the film) is:

$$Q = \frac{KP^* A}{L} \Delta p \quad (1.6)$$

Where:

- Q : permeation rate at steady state;
- KP : permeability, defined as the product of diffusion coefficient and solubility coefficient;
- A : surface area of the film;

- L: thickness of the film;
- Δp : partial pressure difference on the sides of the film.

The permeation rate equation describes the permeation rate as a function of package and environmental variables. The package variables include permeability KP and packaging dimensions (A and L). The environmental variables include Δp . Temperature and relative humidity are implicitly included in permeability. KP is also function of temperature (Lee et al., 2008).

1.4.6 Water Vapour Transmission Rate

The primary quality deterioration factor of moisture depending products is the absorption of moisture. The essential packaging function required for these products is to slow down significantly the transfer of water vapor from the outside to the inside of the packaging.

To reduce the weight loss, to maintain optimal structure of foods and to limit the increase of water activity that may lead to undesirables reactions the moisture exchanges have to be minimized (Labuza, 1968).

The protection of the package against the moisture transfer depends, besides the barrier properties of the materials used, also on the integrity of the package and on the seal strength and sealing systems. There are several factors that can influence the permeation of gases or vapors. Some are intrinsic, such as the chemical nature of the material, other extrinsic, such as environmental conditions. Among these temperature is the factor that, maintaining constant the thickness, the surface area available to diffusion and the driving force, has the most influence on the permeation phenomena. The permeability (KP) dependence towards temperature (Paine & Paine, 1992) is of exponential type, as described by the Arrhenius equation:

$$KP = KP_0 * e^{\frac{-E_a}{RT}} \quad (1.7)$$

Where:

- KP: permeability constant. Defined as quantity of gas permeating through a unit thickness of a unit surface area in the unit of time for the effect of a unit difference of pressure

$$\left[\frac{g * \mu m}{m^2 * 24h * kPa} \right];$$

- KP_0 : pre-exponential constant. Represents KP at infinite temperature $\left[\frac{g * \mu m}{m^2 * 24h * kPa} \right];$

- E_a : permeation activation energy. Given by the sum of the diffusion activation energy and the heat of dissolution for the coefficient of solubility $\left[\frac{J}{mol} \right];$

- R: universal gas constant $\left[8.314 \frac{J}{K * mol} \right]$;
- T: absolute temperature $[K]$.

The temperature influence in a water vapor permeability measure is more complex than the permeability measure to permanent gases such as atmospheric O₂, N₂, and CO₂. In the case of water vapor a temperature increase changes the diffusivity and solubility of the permeated matrix but also increases the driving force of the permeation (Fava, 1996).

This temperature dependence is significant and it is an exponential type relation, described by the Clausius Clapeyron equation:

$$WVP = p^* \exp \left[-\frac{\Delta H_{evap}}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right) \right] \quad (1.8)$$

Where:

- WVP: water vapour permeation $\left[\frac{g * \mu m}{m^2 * 24h * kPa} \right]$;
- p *: vapour pressure of water at the triple point $[Pa]$;
- T *: temperature of water at the triple point $[K]$;
- ΔH_{evap} : molar enthalpy of vaporization;
- R: universal gas constant $\left[8.314 \frac{J}{K * mol} \right]$;
- T: absolute temperature $[K]$.

In literature it is more common to find tables that show the values of vapour pressure at different temperatures rather than the integrated form of this equation.

A further complication that occurs in packaging materials is that the inverse proportionality between the permeability and thickness is not always verified. Therefore the difference in vapour pressure and the thickness are not considered in the calculation of the permeability but are referred as measurement conditions. This leads to the definition of a new property defined, in the case of water vapor transmission, as Water Vapor Transmission Rate (WVTR).

This new property defines the quantity of water vapour permeating through a unit surface area of given thickness at specific conditions of temperature and relative humidity on both sides of the material, in unit time. Its units are therefore (ASTM, 1994):

$$\left[\frac{g}{m^2 * 24h} \right]$$

In literature WVTR values measured in tropical conditions are available, determined at 38°C and 90% RH. In these conditions the driving force of the phenomena is 5.96 kPa (44.7 mHg). The knowledge of the water vapour transmission rate of flexible packaging materials is essential to predict the shelf life of moisture sensitive products (Labuza,1982; De Leiris, 1986).

1.5 Shelf life

Shelf life is defined as the period of time during which a food retains acceptable characteristics of flavor, color, aroma, texture, nutritional value, and safety under defined environmental conditions. It is also encompasses the time during which a product may reasonably be expected to meet its label claims for specific attributes (Lee et al., 2008).

Establishing the shelf life of many food products can be expensive and time-consuming. It is essentially a process of informed trial and error, and the only really effective way to establish shelf life is to keep the product under typical storage conditions until spoilage occurs.

In most real life situations of new product introductions or existing product changes, time limitations in research and development preclude from conducting shelf life testing. In practice, different approaches can be utilized for shelf life estimation but real shelf life tests and accelerated shelf life testing are the common way to define the expiration date of a food product.

However there are models that can be used to save a significant amount of time and expenses helping to predict what the shelf life will be. Used correctly, these models allow to reduced product development times and costs, with a lower time to market.

1.5.1 Shelf life testing

Shelf life testing is classic technique of prediction. It consists in monitoring the changes in quality during the supply chain, real or simulated, in order to identify the attributes of interest, to identify the primary events of degradation and the measures to be taken to counter them.

In the case of products in which the primary degradation event is the exchange of moisture with the environment, this technique requires the storage of the product packages in different temperature and moisture situations for long periods of time to simulate the real conditions of storage.

This method has the advantage that it reproduces faithfully the conditions of storage obtaining reliable results, but it has two drawbacks: long execution times (for some products it may take up to ten or twelve months), and the immobilization of a large amount of references.

To determine the value at which corresponds the end of the shelf life of a product it is important to perform product sensory tests at different conservation times during the storage. These tests have to be done by a panel of expert and trained tasters. A comparison of the overall evaluation of these tests with the analytical parameters measured will allow defining the shelf life.

This approach is known as the "Profile Attribute Analysis". It consists in giving votes to the different attributes based on numerical scales and to report them into a column to form a path defined as the "profile". The evaluation of the same attributes over time allows the panel to define the degradation of the various attributes considered that are influenced by the combined effect of the environmental and natural aging. The reach of limit values for the attributes defines the shelf life standards and the recommended maximum consumption limit (Robertson, 1993).

1.5.2 Accelerated shelf life testing

During the development a new product one of the aspects that most delay the process is the need to wait the results of shelf life test carried out on the samples.

One technique that can improve this part of the development is based on the laws of chemical kinetics that correlate the rate of a reaction with the temperature at which it takes place. Storage at more severe conditions than the real ones can be used, such as higher temperatures, higher relative humidity or exposure to light (Labuza & Schmidl, 1985). This method is useful only if the accelerating factor introduced by the conditions of accelerated aging is known exactly. The shelf life is extrapolated through a mathematical model, provided that the factor responsible for decay acceleration, introduced with the critical conditions, is well known. Results obtained with these approaches refer only to the particular product studied in its package, so the tests are not much flexible.

1.5.3 Shelf life models

As an alternative to these methods, the optimal packaging solution can be determined by means of mathematical models of prediction, in which all the variables associated to the product, the package and the ambient conditions are considered. This approach allows more flexibility, since different packaging solutions can be tested in short times (Fava et al., 2000).

Shelf life models are mathematical equations which describe the relationship between food, package, and environment. The first study dealing with prediction models dates back to the fifties (Heiss, 1958),

Shelf life models are useful to predict the shelf life of food, to design food packages, and to provide useful insights. The accuracy with which these relationships are measured influences the reliability of the models. It is also necessary to know the relationships among the variables that play a significant role in defining food quality.

1.5.3.1 Temperature depending models

The most diffuse shelf life predictive models are based on the knowledge of food temperature exposure. Temperature is the characteristic of the distribution environment that has the greatest impact on the storage life and safety of fresh perishables. Effective temperature management is in fact, the most important and simplest procedure for delaying product deterioration (Nunes et al., 2006).

One very common approach is to describe the quality decay according to the law of Arrhenius for reaction kinetics. The change in shelf life or loss per day is calculated as a function of temperature (Jedermann et al., 2006).

For many food products, a chain of chemical or enzymatic processes contribute to a loss of quality. The approximation by one or two Arrhenius functions does not always deliver the required accuracy. For a precise prediction the time function of several quality factors like color, firmness, mould and C vitamin content, have to be estimated. Because it is not possible to know in advance which of the curves will be the most critical one, all of them have to be continuously calculated and monitored. Descriptions of the underlying chemical reactions by a set of differential equations are only known for a minority of products. In many cases only tables for different constant temperatures are available, listing the change of physical properties over time. To extract a set of differential equations from these measurements requires expert chemical knowledge that is in general not available. The suggested table-shift approach provides a prediction for dynamic temperature condition based on curves recorded at constant temperatures. The value of each physical property for the next step is read out from the pre-measured table. If the temperature changes, the focus in the table is shifted to the row that matches the current quality inside the column for the new temperature. In the mathematical description the change of a physical property is calculated as a two dimensional interpolation over the parameters temperature and current property state. The table-shift approach provides a method for a direct calculation of the shelf life based on a set of measured

reference curves. The accuracy of this approach has to be validated for new product types by comparison of simulated curves for dynamic temperature conditions with measured data (Jedermann et al., 2007).

1.5.3.2 Moisture depending models

Many chemical, biological, and physical changes are dependent on moisture content or water activity in foods, whose changes may be dictated by the packaging protection from the environment in the distribution channel.

Many authors proposed different mathematical models in which the moisture sensitivity of the food and the package performances were combined differently (Iglesias et al., 1979; Labuza & Contreras-Medellin, 1981; Tubert & Iglesias, 1985; Del Nobile et al., 2003).

The simulation models are theoretically based on the relationship between moisture uptake of food product, storage environment and barrier property of packaging material (Hernandez & Giacini 1997; Azaña & Faria 2005).

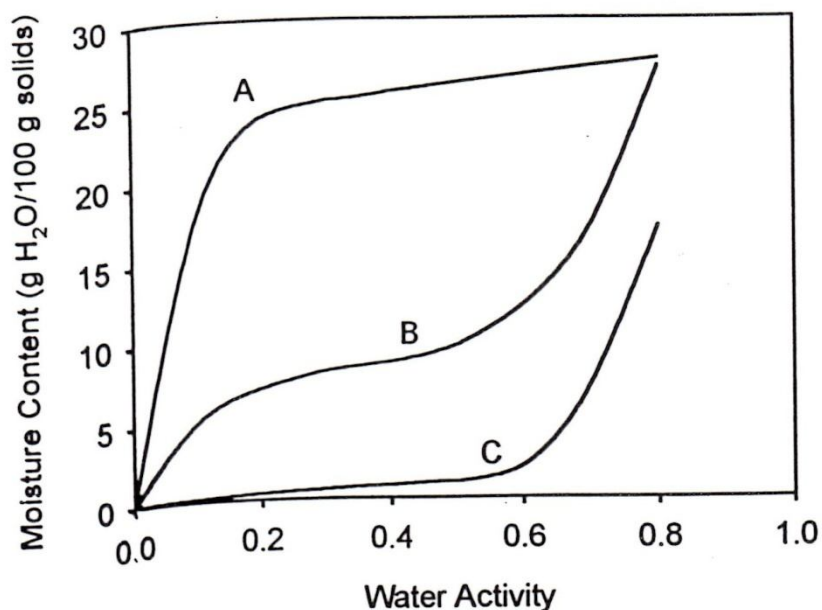
Water activity is ruled by the moisture content in the food, which may change with time through the permeation process of water vapor across the packaging film. The equilibrium relationship between moisture content and water activity is explained by the sorption/desorption isotherm, which is obtained mostly by the experiments determining moisture contents of the food samples equilibrated under different relative humidity conditions.

Moisture sorption isotherms of food products are useful to determine their storage stability as well as to predict their shelf-life since they give information about the equilibrium relationship between product moisture content and water activity, at a given temperature and relative humidity (Palou et al., 1997; Vijayalakshmi, 2005; Togrul & Arslan, 2007).

Since foods are complex in nature, mostly multicomponent and multiphase systems with internal intricate structure, the equilibrium moisture sorption isotherms are an intrinsic property of the material.

In Figure 1.3 is shown the isotherm classification of Brunauer et al. (1945).

Figure 1.3: isotherm classification.



Classification of moisture sorption isotherm (Brunauer *et al.*, 1945).

- A: type I, anticaking agents;
- B: type II, most foods;
- C: type III, crystalline substances.

Foods show essentially two different types of isotherms, the sigmoid type typical of most foods, including low moisture foods, and the gradually increasing type, less frequently seen (Lewicki, 1998). These are type II and III isotherms according to the classification of Brunauer *et al.* (1940).

Determination of the optimal equation to fit the experimental isotherm data is crucial for representing the relationship between the equilibrium and water activity of food products. The major considerations in equation selection are food characteristics, simplicity and suitability for application over the range of water activity of interest (Hayoglu & Gamli, 2007).

The most widely used equations used to express the equilibrium relationship by mathematical forms are the ones developed by Smith, Halsey, Henderson, Oswin, Inglesias, and Chirife (Lee *et al.*, 2008). These equations are used in forecast models to determine the shelf life of moisture depending products.

Moisture depending shelf life models are based on two main hypotheses: the water vapour present in the headspace of the packaging (which changes with the entrance of water vapour from the outside) is always immediately in equilibrium with the product and the water vapour present in the package headspace behaves as an ideal gas (Quast & Karel, 1972; Bell & Labuza, 2000).

The first condition that states the immediate equilibrium of the water vapour has not been verified experimentally and is based on theoretical considerations (Fava *et al.*, 2000).

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2 Aim of the research

The aim of this PhD thesis is the study of innovative approaches and instruments to model and monitor the shelf life of packaged perishable foods.

The crucial part of this work is to verify the theoretical assumption of immediate equilibrium assumed by moisture depending prediction models. This assumption states that the relative moisture of the headspace of the packaging (which changes with the entrance of water vapour from the outside) is immediately in equilibrium with the product (Quast & Karel, 1972; Bell & Labuza, 2000; Fava et al., 2000).

To achieve this result it is necessary to develop and build an acquisition system based on sensors, a recording unit and specific software to collect data on physical indexes of food quality for defined products, and to measure them. This system has to be tested on different products and packages in order to define the proper materials and working conditions to define the experimental plan and the system settings.

Furthermore, the model system has to be used to study how different quantities of product, different headspace volumes, and different packaging solutions influence the equilibrium between the relative humidity of the headspace and of the product and how these differences influences the shelf life prediction.

On the basis of the collected data, existing shelf life prediction models must be verified and, if needed, modified in order to predict the shelf life of products.

A subsequent part of the work will consider the possibility to simplify the shelf life prediction for a category of products applying a unique shelf life model for all the products that are part of the category.

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3 Materials and methods

3.1 Materials

3.1.1 Apple rings

Organic apples cv 'Golden Delicious' grown at the Research Centre for Agriculture and Forestry (Laimburg, BZ, Italy) were used for the shelf life study. Apples were washed, wiped dry and cored by a spoon soil auger (25.0 mm diameter) and they were mechanically cut into 5.0 mm thick rings (LT INOX, Kronen, Germany).

Immediately after cutting the apple rings were air dried. Air drying was performed at 82°C, up to constant weight, using an alternate upward-downward air circulated drier (ThermoLab, Lodi, Italy), operating at an air speed of 1.5 ms⁻¹, with a load of 2.7 kgm⁻². The equilibrium weight (i.e. the constant weight) was achieved when the difference in weight was less than 1 mg/g solids after 30 additional minutes of drying.

Figure 3.1: dried apple rings.



The apples had a starting moisture content expressed as grams of water content in the product for grams of dry basis of 84.47 g H₂O/g db and a water activity of 0.99.

At the end of the air drying process the moisture content was of 2.78 g H₂O/g db and the water activity of 0.125 (Gobbi, 2009).

In Table 3.1 are reported the air drying time and the percentage weight loss of the apple rings during the air drying.

Table 3.1: apple rings weight loss during air drying.

Time [min]	Weight [%]
0.01	100
60	22.568
90	17.096
120	16.106
150	15.832
180	15.743
210	15.687
240	15.658
270	15.626
300	15.626

3.1.2 “Fetta biscottata”

“Fetta biscottata”, a typical Italian bakery product, has been chosen for the present work because of its regular shape and geometry, and the uniformity among different packages. The acceptable maximum moisture content for the consumption has been set at a relative humidity (RH) of 40%.

14 different types and brands of “Fetta biscottata” have been bought in different supermarkets in the city of Milano. In Table 3.2 are reported the codes assigned to each of the 14 types of “Fetta biscottata” (Figure 3.2 to Figure 3.15) and the commercial descriptions. In Table 3.3 and Figure 3.16 are reported the nutritional values of the samples declared by the producer.

Table 3.2: codes and commercial descriptions of “Fetta biscottata”.

Sample number	Commercial description
1	Dorate
2	Cereali
3	Integrali
4	Classiche
5	Integrali
6	Biscotto salute
7	Fette iposodiche
8	Fibreextra integrale
9	Malto d'orzo
10	Grano saraceno
11	0,02% sodio
12	Classiche
13	Integrali
14	Integrali

Figure 3.2: sample 1 "Dorate".



Figure 3.3: sample 2 "Cereali".



Figure 3.4: sample 3 "Integrali".



Figure 3.5: sample 4 "Classiche".

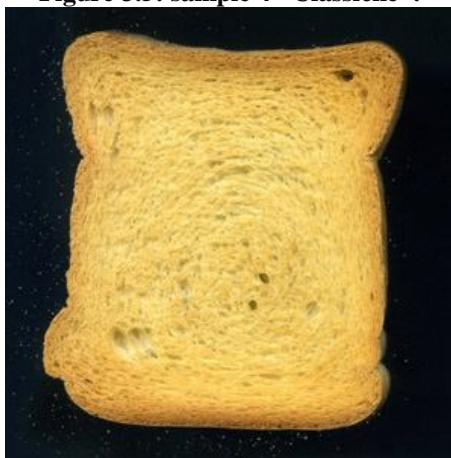


Figure 3.6: sample 5 "Integrali".



Figure 3.7: sample 6 "Biscotto salute".

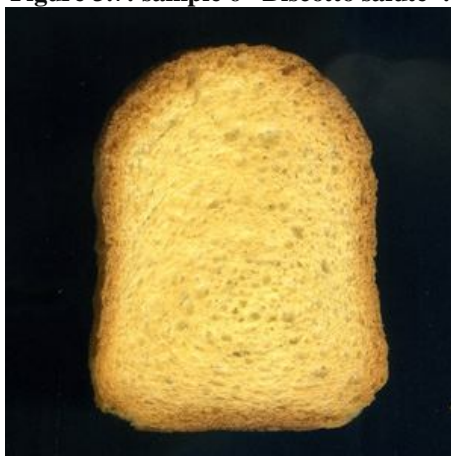


Figure 3.8: sample 7 "Fette iposodiche".

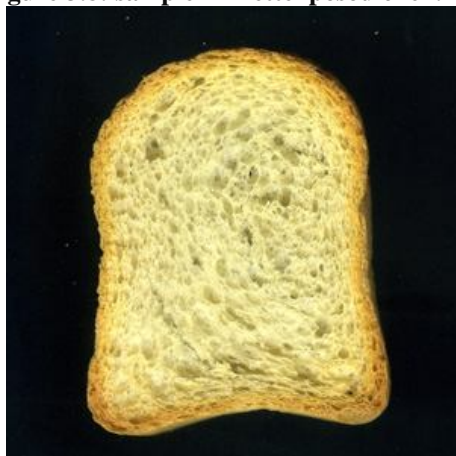


Figure 3.9: sample 8 "Fibreextra integrale".

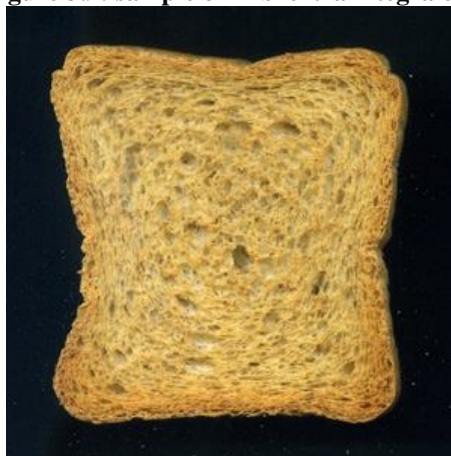


Figure 3.10: sample 9 "Malto d'orzo".



Figure 3.11: sample 10 "Grano saraceno".



Figure 3.12: sample 11 "0,02% sodio".

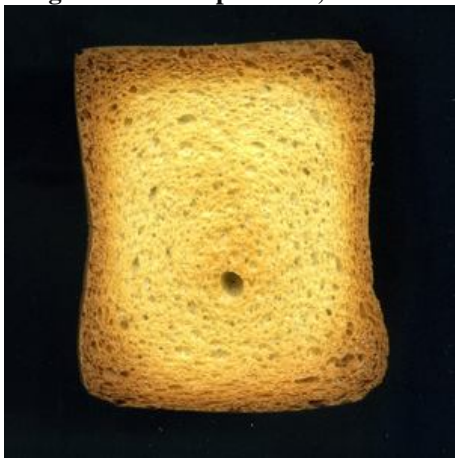


Figure 3.13: sample 12 "Classiche".

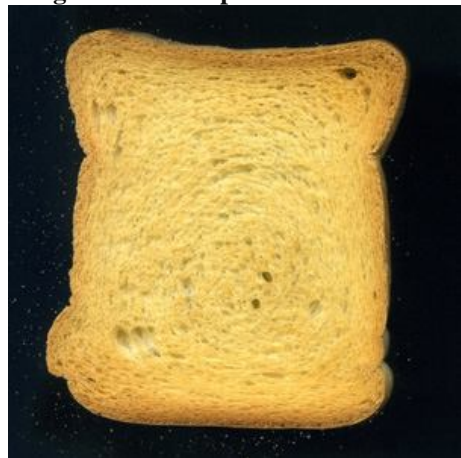


Figure 3.14: sample 13 "Integrali".



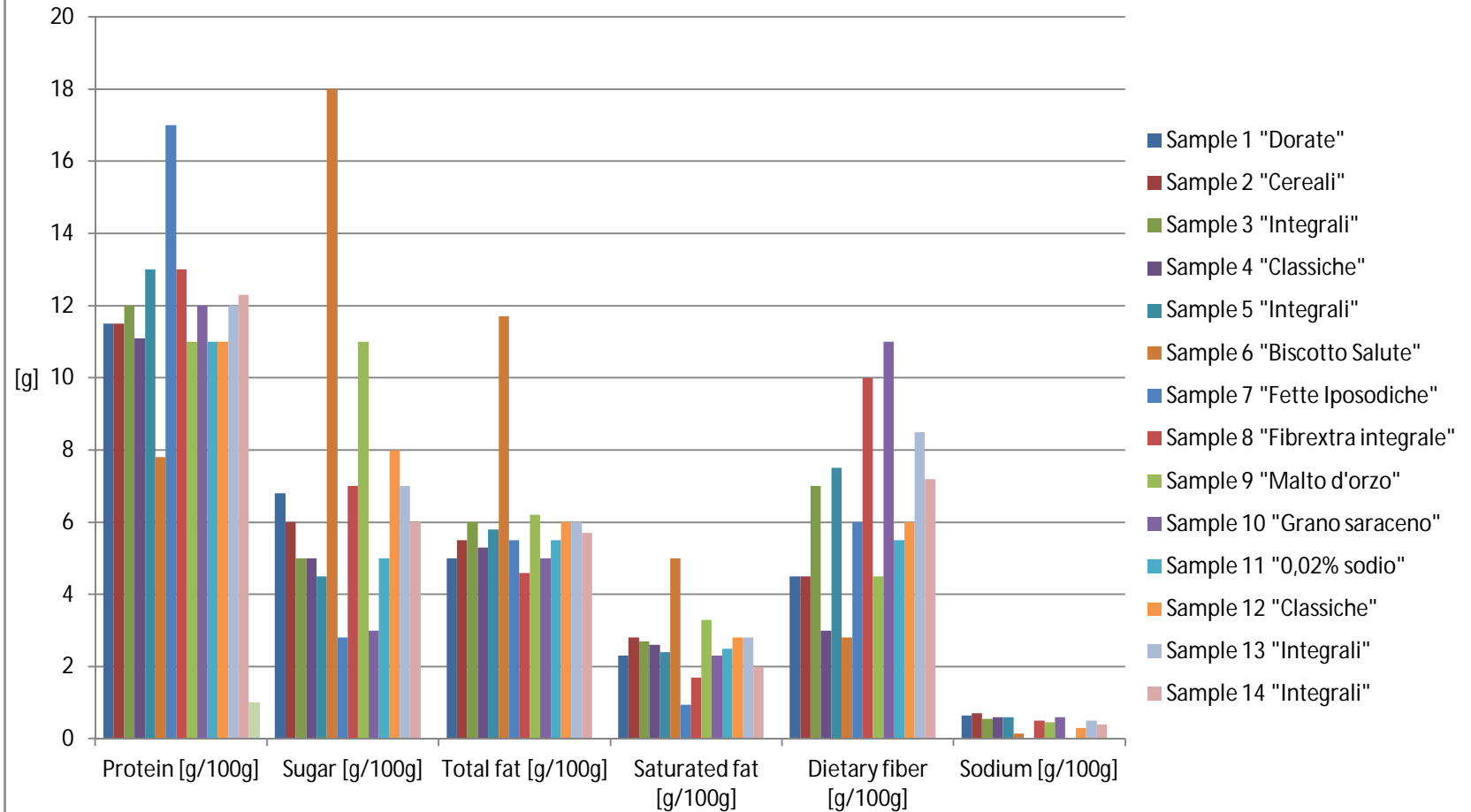
Figure 3.15: sample 14 "Integrali".



Table 3.3: nutritional values of the samples declared by the producer for “Fetta biscottata”.

Sample	Protein [g/100g]	Sugar [g/100g]	Total fat [g/100g]	Saturated fat [g/100g]	Dietary fiber [g/100g]	Sodium [g/100g]	Energetic value [kJ/100g]	Carbohydrate [g/100g]
Sample 1 "Dorate"	11.5	6.8	5	2.3	4.5	0.65	1675	74
Sample 2 "Cereali"	11.5	6	5.5	2.8	4.5	0.7	1679	73.2
Sample 3 "Integrali"	12	5	6	2.7	7	0.55	1667	69.7
Sample 4 "Classiche"	11.1	5	5.3	2.6	3	0.6	1713	76.7
Sample 5 "Integrali"	13	4.5	5.8	2.4	7.5	0.6	1587	67.7
Sample 6 "Biscotto salute"	7.8	18	11.7	5	2.8	0.15	1854	74.5
Sample 7 "Fette iposodiche"	17	2.8	5.5	0.95	6	0.02	1635	67.2
Sample 8 "Fibre extra integrale"	13	7	4.6	1.7	10	0.5	1602	66.5
Sample 9 "Malto d'orzo"	11	11	6.2	3.3	4.5	0.45	1717	74.4
Sample 10 "Grano saraceno"	12	3	5	2.3	11	0.6	1611	66.7
Sample 11 "0,02% sodio"	11	5	5.5	2.5	5.5	0.02	1676	73
Sample 12 "Classiche"	11	8	6	2.8	6	0.3	1642	72.5
Sample 13 "Integrali"	12	7	6	2.8	8.5	0.5	1582	68
Sample 14 "Integrali"	12.3	6	5.7	2	7.2	0.4	1602	69.5

Figure 3.16: nutritional values of the samples declared by the producer for fetta biscottata.



3.1.3 Packaging materials

OPP film produced by Moplefan, the thickness was 20 μm with a water vapour transmission rate of $2.505 \pm 0.035 \text{ g m}^{-2} 24\text{h}^{-1}$ at 25°C and 90%RH.

Rigid EPS trays produced by Sirap Gema (Italy). 2 different volumes were selected: 1400 and 1030 cm^3 .

Rigid EPS trays sealed with an OPP film have been used as a model package system.

3.1.4 Acquisition system

To monitor and record the relative humidity values an acquisition system has been developed and built in collaboration RDE Company srl (Novate Milanese, Milano).

The system was composed by:

- personal computer (ASUS, Taiwan);
- specific software application based on National Instruments LabVIEW 8 (Austin, TX, USA) to collect and record measured values;
- data acquisition module by National Instruments NI USB-6211, with USB power supply and data connection and 16 analogical acquisition channels (16-bit, 250 kS/s);
- 15 sensors model HIH 4000-001 Series Integrated Circuitry Humidity Sensor by Honeywell (Morristown, NJ, USA);
- plastic boxes (Piazza, Crusinallo, VB, Italy) with a capacity of 8 liters with an hermetic lid. Each box was equipped with a terminal to connect the sensors and a fan (Multicomp, Montfoort, Benelux) with a power supply of 5V e 0.07A to stir the air inside the box.

The sensors model HIH 4000-001 Series Integrated Circuitry Humidity Sensor by Honeywell had the following characteristics:

- precision: $\pm 3.5\%$ RH;
- temperature range relative: from -40°C to 85°C;
- relative humidity range: from 0% to 100%;
- linearity: $\pm 5\%$ RH from 0 to 60% RH and $\pm 8\%$ RH from 60% to 100% RH;
- stability: $\pm 0.2\%$ RH in 12 months at 50% RH;
- hysteresis: maximum $\pm 3\%$ RH.

Figure 3.17: acquisition system layout.

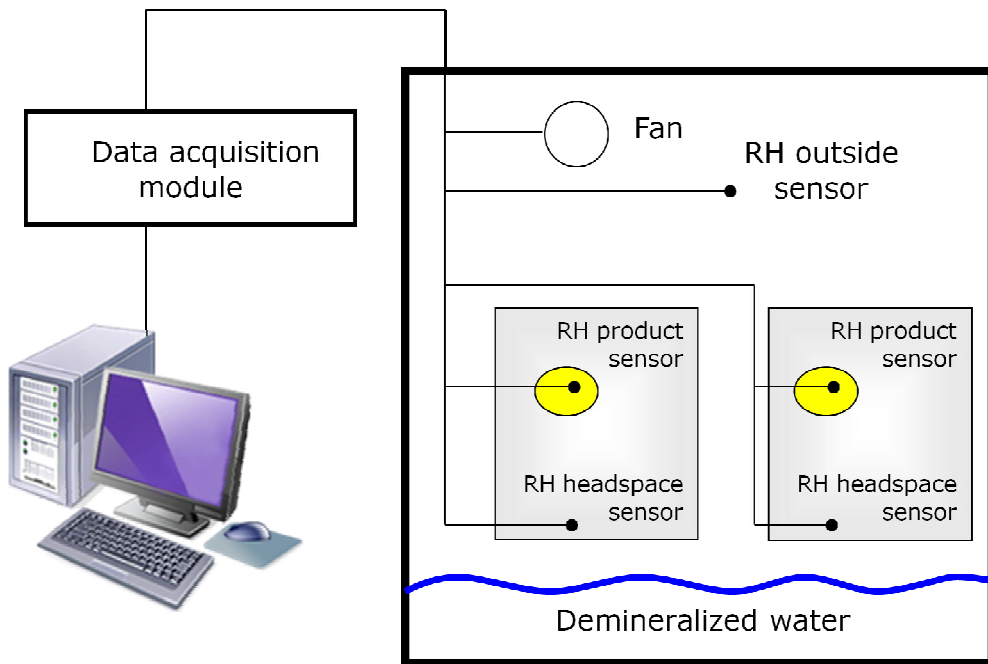


Figure 3.18: box equipped with sensors and fan.

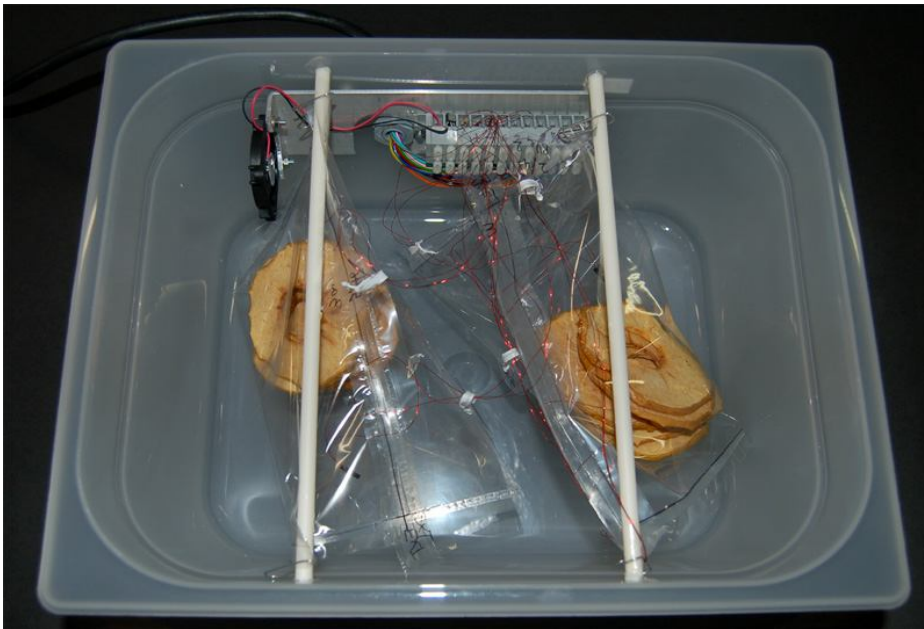
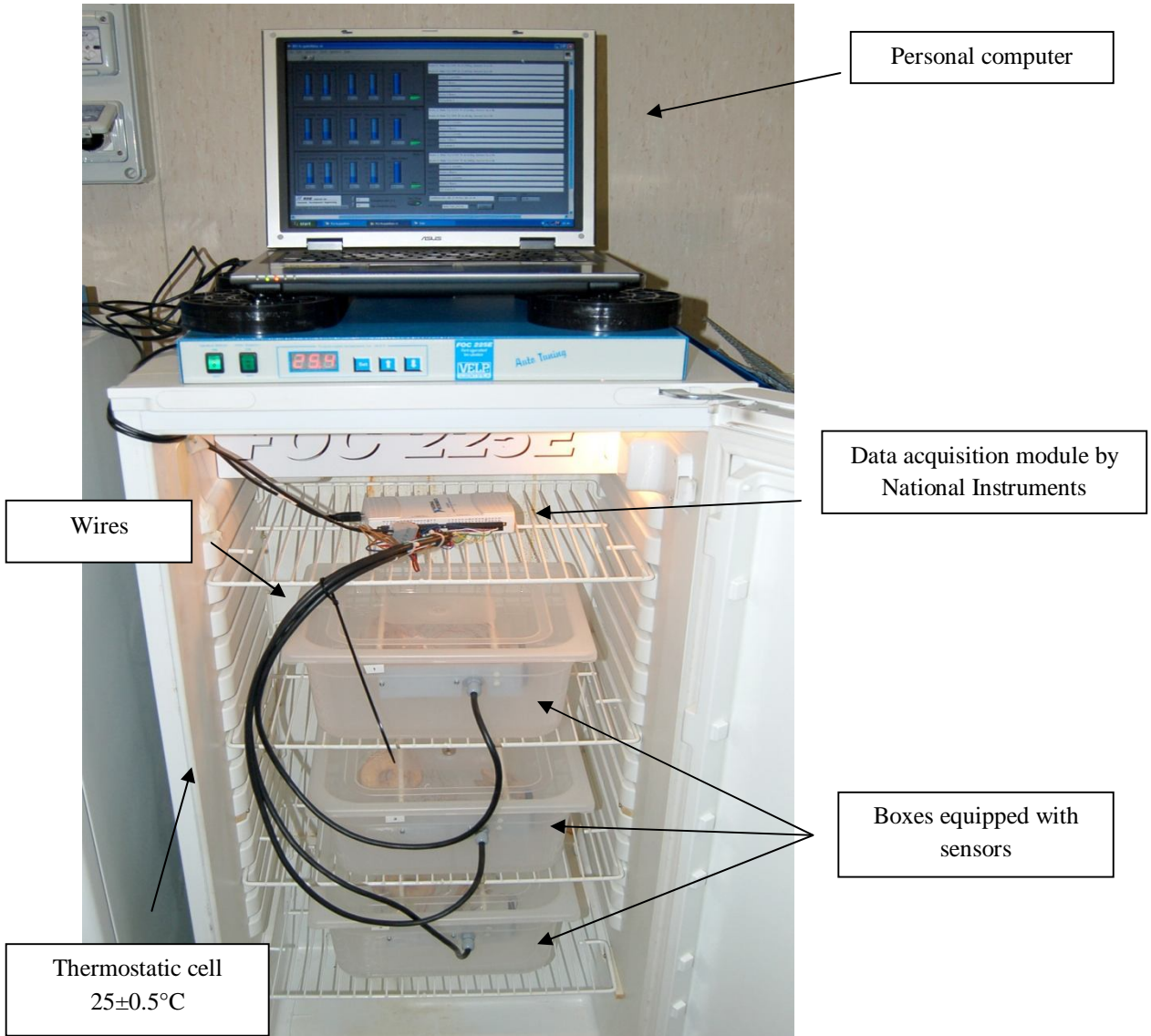


Figure 3.19: Acquisition system in working conditions.



3.2 Methods

3.2.1 Water activity measures

The water activity (a_w) of “Fetta biscottata” and of the saturate salt solutions was measured at $25\pm 0.2^\circ\text{C}$ with a Novasina LabMaster a_w (Novasina AG, Switzerland);

The samples were placed inside the instrument and the value was recorder when the temperature and the water activity value were both constant for at least a five minute interval.

3.2.2 Moisture content

The moisture content (M) was determined in an oven (Termostabili C₃ Ovenlab, Cavallo srl, Buccinasco, Italy) at 130°C for 1.5 h. The moisture content is expressed as grams of water content in the product for grams of dry basis [g H₂O/g db].

3.2.3 Water vapour transmission rate of the packages

The water vapor transmission rates of the packages has been measured with a static gravimetric method (Lee et al., 2008). Known quantities of calcium chloride dehydrate have been sealed inside the packages. The packages have been placed in sealed plastic boxes (Giostyle, Urganio, Italy) with a volume of 6 liters and dimensions of 30x25x15 cm. On the bottom of each box was present 1 liter of demineralized water to obtain a moisture content of 100% inside the box. The boxes were stored in a climatic chamber (FOC 225) at 25°C . Every 48 hours the weight of the boxes has been recorded and, after a period of 4 weeks, the water vapour transmission rate of the packages has been determined considering the increase of weight (water permeated through the package and adsorbed by the calcium chloride dehydrate) in time.

To verify if the presence of the sensor wires in the sealing affected the permeability of the package 3 boxes were sealed without the wires (Figure 3.20), 3 with the wires (Figure 3.21).

Figure 3.20: package without wires.

Figure 3.21 package with wires.



3.2.4 Shelf life testing

Shelf life tests have been carried out at the PackLab at DISTAM (Università degli Studi di Milano, Via Celoria 2, Milano, Italy). The packages have been placed in sealed plastic boxes (Giostyle, Urganano, Italy) with a volume of 6 liters and dimensions of 30x25x15 cm. On the bottom of each box was present 1 liter of demineralized water to obtain a moisture content of 100% inside the box. The boxes were stored in a climatic chamber (FOC 225) at 25°C.

3.2.5 Sorption isotherms determination

Water vapour sorption isotherms were determined according to the static, gravimetric method developed by COST-90 Project, and reported by Wolf et al. (1985). The principles were described by Bell and Labuza (2000).

“Fetta biscottata” were placed in sealed plastic boxes (Giostyle, Urganano, Italy) with a volume of 6 liters and dimensions of 30x25x15cm. 3 “Fetta biscottata” were placed in each box containing saturated salt solutions and stored in a climatic chamber (FOC 225) at 25°C.

The water activity (a_w) of these solutions was in the range of 0.114-0.841. Salt used and their water activity value at saturation are shown in Table 3.4.

Table 3.4: inorganic salts used to prepare the saturated solutions and corresponding water activity at 25°C.

Salt	a_w
Lithium chloride anhydrous	0.114
Potassium acetate	0.241
Magnesium chloride hexahydrate	0.331
Potassium carbonate anhydrous	0.438
Magnesium nitrate hexahydrate	0.529
Lithium acetate dihydrate	0.691
Sodium chloride	0.753
Potassium chloride	0.841

Samples were weighed every five days and the equilibrium was considered to be reached when the change in weight did not exceed 0.1% in 2 consecutive weightings at no less than five-day intervals (Biquet & Labuza, 1988). The equilibrium for “Fetta biscottata” was reached in twenty-five days.

The final moisture content of each sample was calculated with the formula:

$$M = \frac{[w_2 - w_1] + \frac{\%H_2O}{100} \times w_1}{w_1 \times \left[\frac{100 - \%H_2O}{100} \right]} \left[\frac{gH_2O}{gdb} \right] \quad (2.1)$$

Where:

- w_1 : initial product weight [g];
- w_2 : final product weight [g];
- $\%H_2O$: initial moisture content [g/100g] of the product on a wet basis;
- M : product moisture content, expressed as grams of water content in the product for grams of dry basis [g H_2O /g db].

The M values obtained experimentally were fitted with the following mathematical equations expressed as moisture content (M) as a function of water activity (a_w). Table Curve 2D software was used.

$$M = a \times [a_w \times (1 - a_w)]^{(1/b)} \quad \text{Oswin, 1946}$$

$$M = a - [b \times \ln(1 - a_w)] \quad \text{Smith, 1947}$$

$$M = a \times \left(\frac{a_w}{1 - a_w} \right) + b \quad \text{Iglesias-Chirife, 1978}$$

$$M = \left[\frac{-\ln(1 - a_w)}{a} \right]^{(1/b)} \quad \text{Henderson, 1952}$$

$$M = \left(-\frac{a}{\ln a_w} \right)^{(1/b)} \quad \text{Halsey, 1948}$$

3.2.6 Moisture sensor calibration

The saturated salt solutions reported in table 3.5 have been selected to calibrate the moisture sensors. The relative humidity values at 25°C were found in literature (Bell and Labuza, 2000).

Table 3.5: inorganic salts solutions used to calibrate the moisture sensors.

°C	% RH	Salt solution
25	11.3±0.3	Lithium chloride anhydrous
25	22.5±0.3	Potassium acetate
25	32.8±0.2	Magnesium chloride hexahydrate
25	43.2±0.4	Potassium carbonate anhydrous
25	52.9±0.2	Magnesium nitrate hexahydrate
25	81±0.3	Ammonium sulfate
25	93.6±0.6	Potassium nitrate
25	97.3±0.5	Potassium sulphate

Calcium chloride dehydrate has also been used to obtain a relative humidity close to zero and demineralized water to obtain a relative humidity of 100%.

The saturate salt solutions have been prepared according to references (Bell and Labuza, 2000) inside glass jars (Bormioli, Fidenza, PR, Italy) with a volume capacity of 0.25 liters. The jars have been closed hermetically with a sealed cap. The saturate salt solutions have been prepared at 25±0.5°C and maintained at the same temperature in thermostatic cells FOC 225.

Once obtained stable saturated salt solutions and verified the stability of the solutions in time, the water activity of the solutions has been measured with a Novasina LabMaster a_w at $25\pm 0.2^\circ\text{C}$. Obtained values are reported in table 3.6.

Table 3.6: water activity values of the saturated salt solutions.

a_w	Salt solution
0.018 \pm 0.001	Calcium chloride dehydrate
0.11 \pm 0	Lithium chloride anhydrous
0.219 \pm 0.0006	Potassium acetate
0.322 \pm 0	Magnesium chloride hexahydrate
0.434 \pm 0.0006	Potassium carbonate anhydrous
0.523 \pm 0	Magnesium nitrate hexahydrate
0.802 \pm 0.0006	Ammonium sulfate
0.931 \pm 0	Potassium nitrate
0.974 \pm 0.0006	Potassium sulphate
0.992 \pm 0.0006	Demineralized water

Obtained values have been multiplied by 100 to obtain the corresponding values of relative humidity.

For simplicity the RH values reported in table 3.7 have been used in the following discussion.

Table 3.7: values used for the discussion.

%RH	Salt solution
0	Calcium chloride dehydrate
11	Lithium chloride anhydrous
23	Potassium acetate
32	Magnesium chloride hexahydrate
44	Potassium carbonate anhydrous
52	Magnesium nitrate hexahydrate
79	Ammonium sulfate
92	Potassium nitrate
97	Potassium sulphate
100	Demineralized water

Two calibrations have been done. One for the sensors designated to be placed inside the package to record humidity values from 5 to 60 %, and the second for the sensors designated to be placed inside the boxes to record humidity values from 95 to 100%.

For the sensors designated to the packages have been used the following solutions: 0-11-23-32-44-52-79%.

The sensors have been placed inside the headspace of the jar, using a specific and modified cap built especially for this reason (Figure 3.22 and 3.23).

Figure 3.22: cap with sensors for calibration.

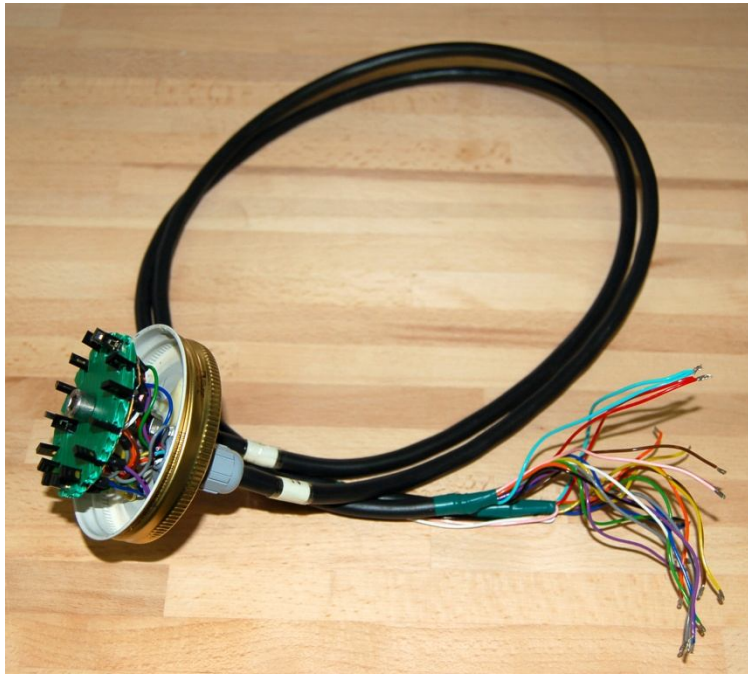
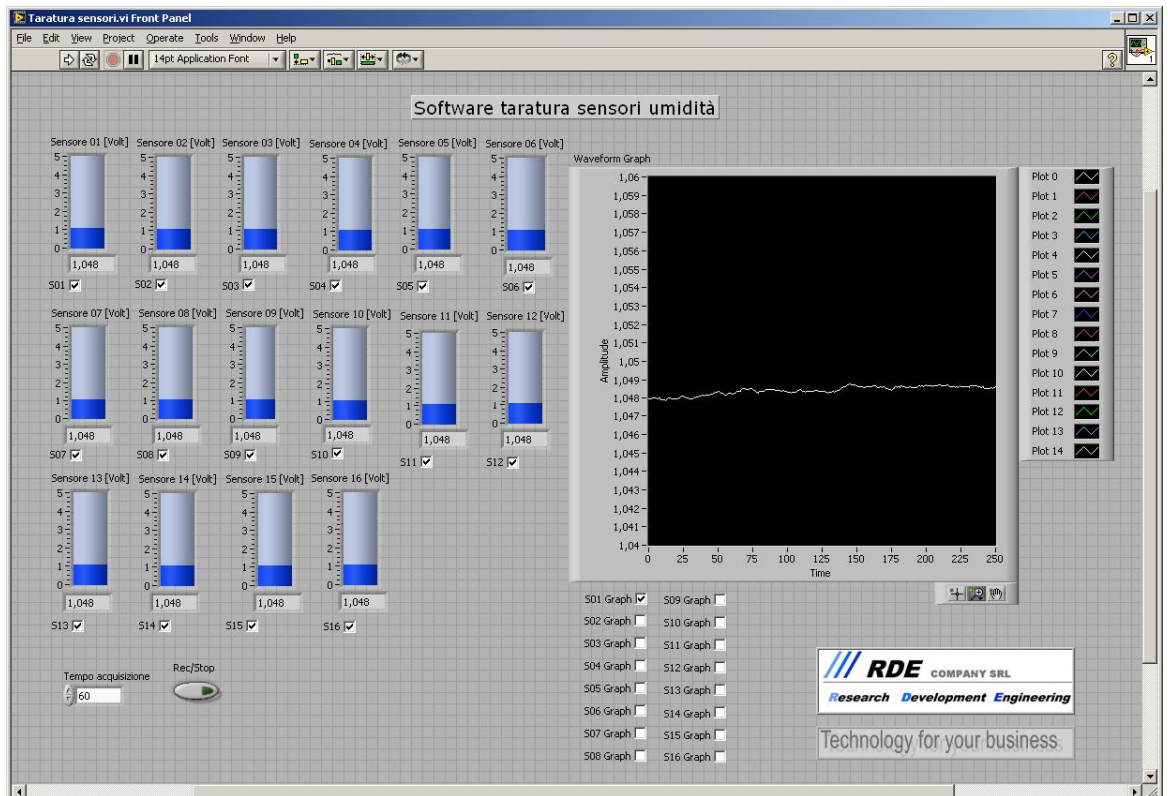


Figure 3.23: jar with sensors in the headspace.



With specific software 16 sensors have been calibrated. The signal of each sensor (Volt output) has been recorded (Figure 3.24).

Figure 3.24: sensor calibration software.



For each sensor the values of voltage and time have been plotted (only the plot of the first sensor is reported for each salt solution).

Figure 3.25: signal of sensor # 1 (RH: 0%) – sampling: 15 minutes.

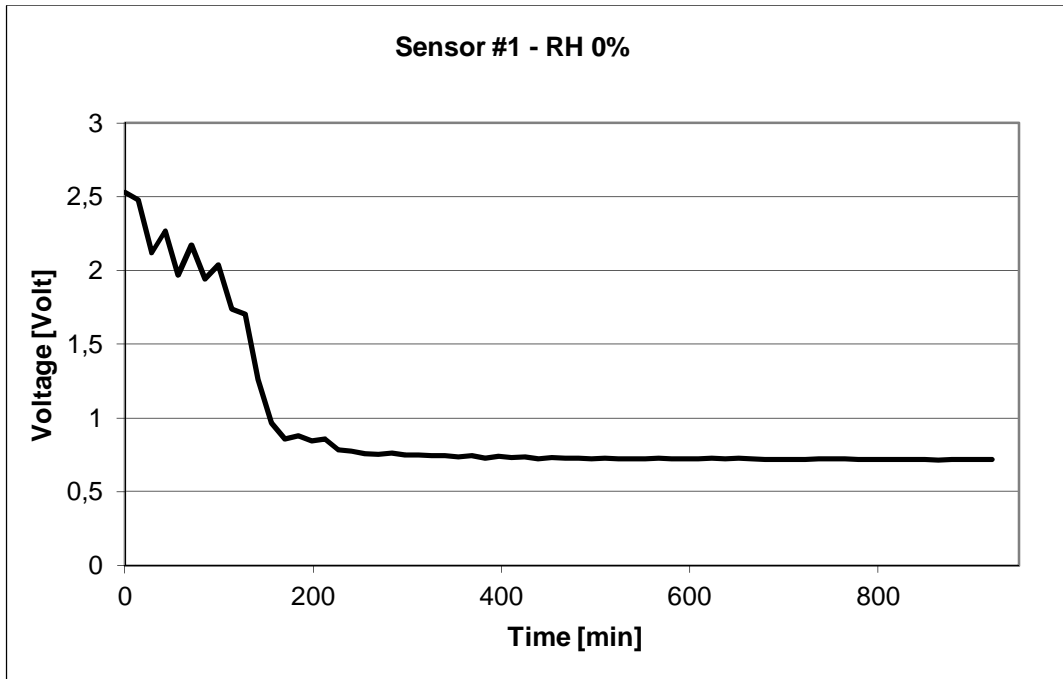


Figure 3.26: signal of sensor # 1 (RH: 11%) – sampling 1 minute.

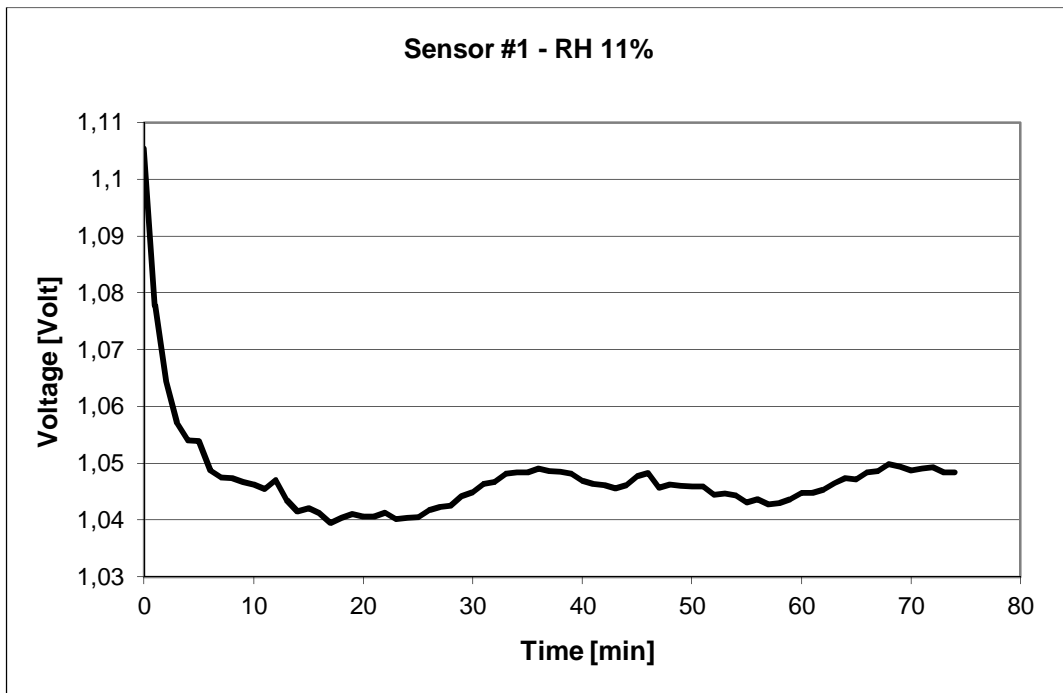


Figure 3.27: signal of sensor # 1 (RH: 23 %) – sampling: 15 seconds.

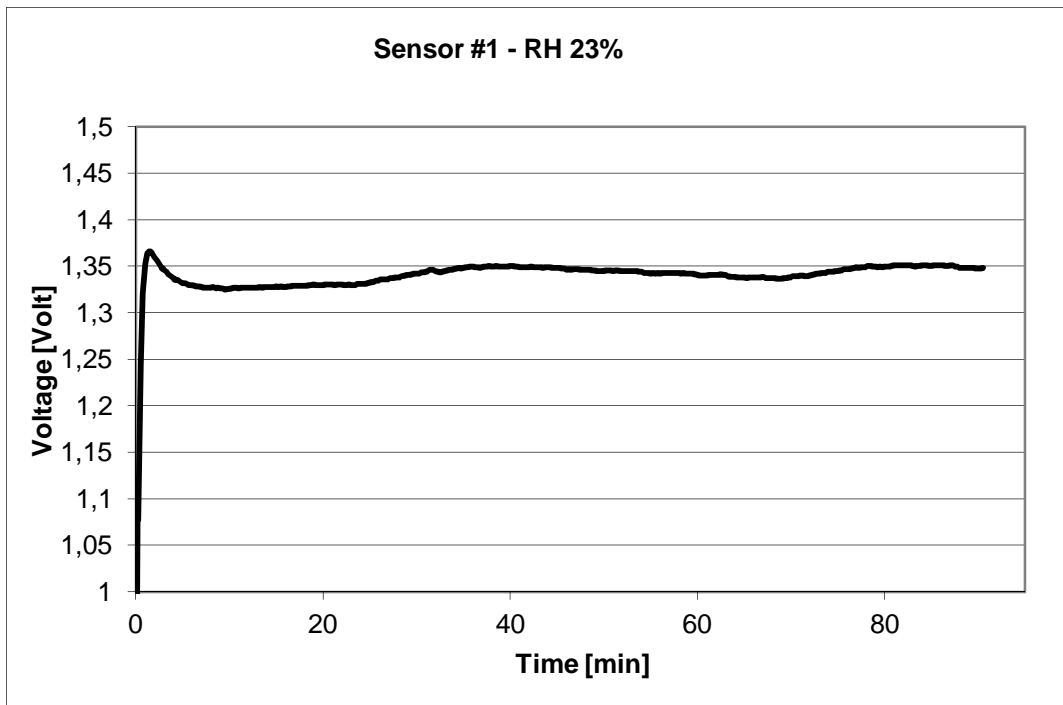


Figure 3.28: signal of sensors # 1 (RH: 32%) – sampling: 1 minute.

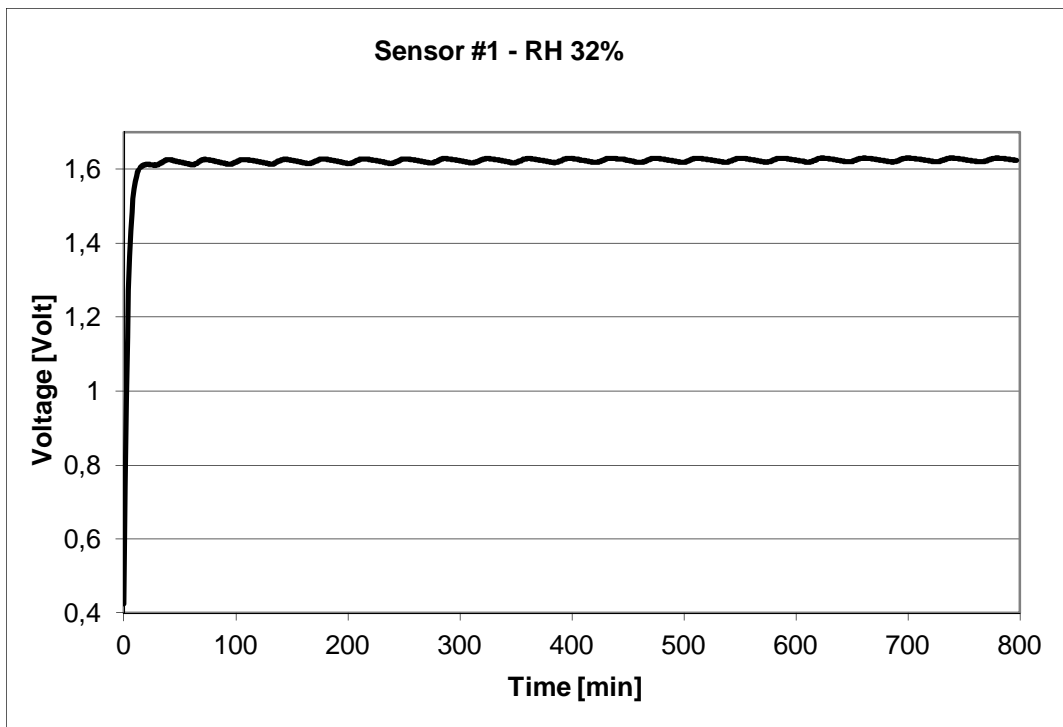


Figure 3.29: signal of sensor # 1 (RH: 44%) – sampling 1 minute.

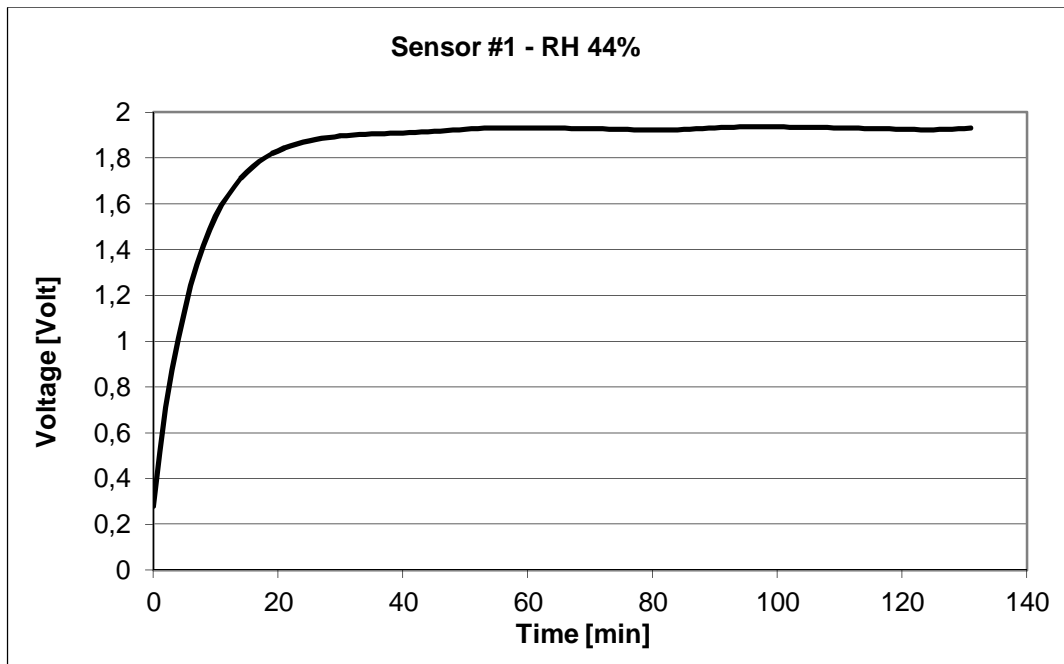


Figure 3.30: signal of sensor # 1 (RH: 52%) – sampling 1 minute.

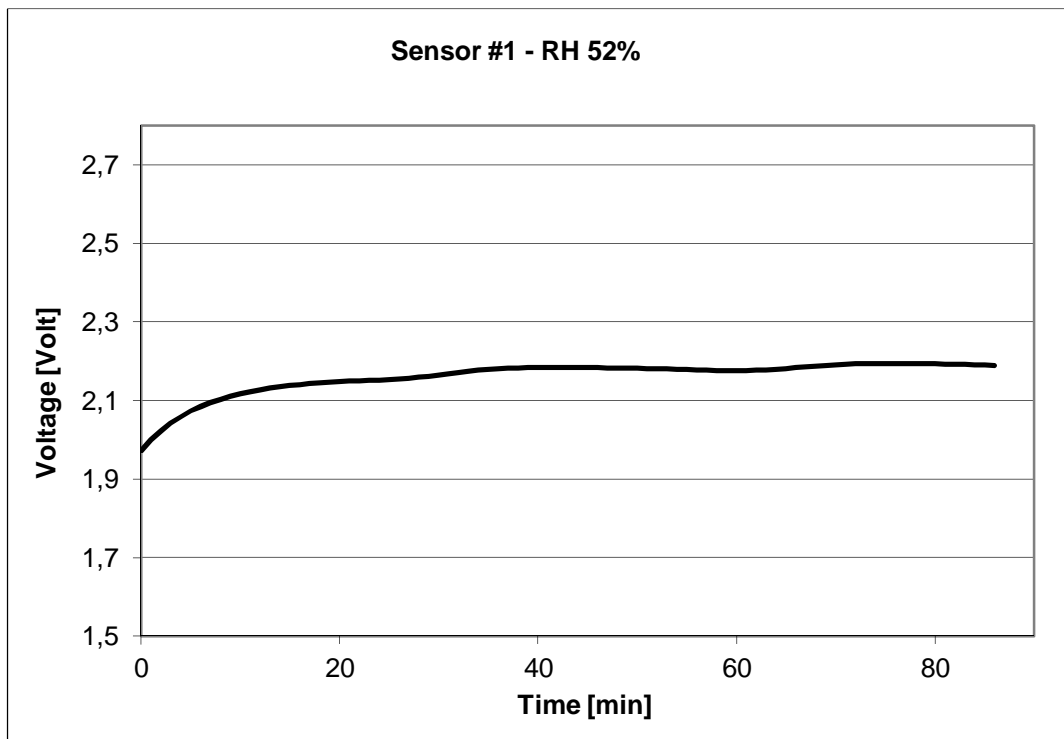
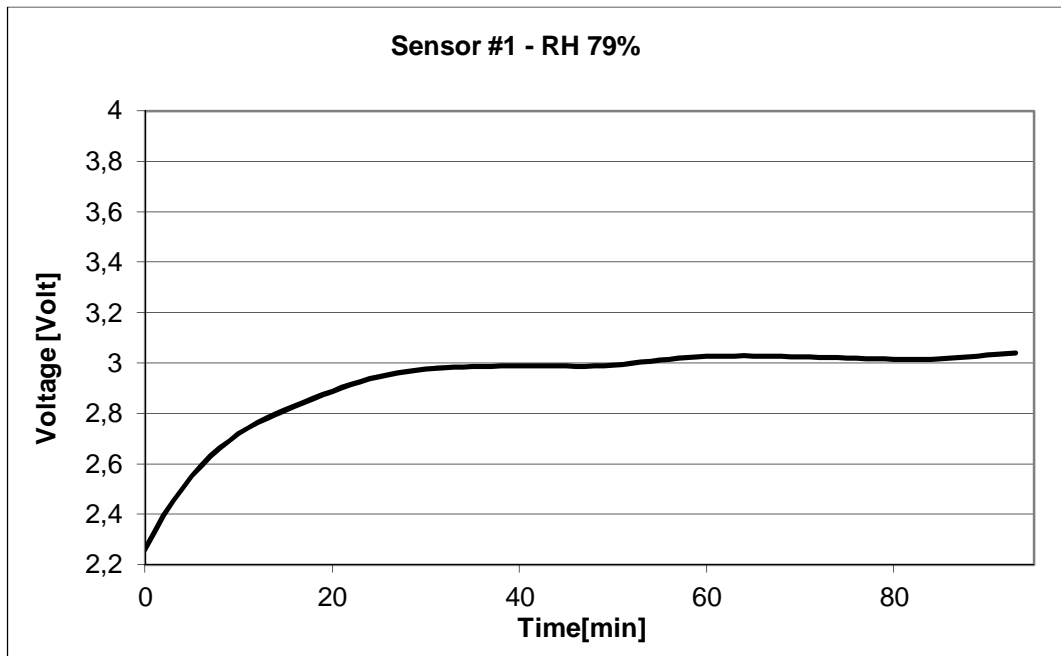


Figure 3.31: signal of sensor # 1 (RH: 79%) – sampling 1 minute.



The values have been recorded with the specific software developed in collaboration with RDE Company. The sampling rate has been selected as the most appropriate for each signal on the basis of the specific characteristics of the output voltage of each sensor.

The scale of the voltage is different for each plot because the most appropriate one to show the signal has been chosen in order to be sure to work at the steady state.

The scale of time is different for each plot because each saturated salt solution has a different equilibrium time. The attainment of the equilibrium before starting the calibration of the sensors is very important. The equilibrium time goes from 30 minutes to 12 hours, depending on the type of salt.

Experience shows that these differences in equilibrium time do not depend on the instrumentation but on the characteristics of the headspace inside each jar, specific for each salt solution.

The fluctuation that can be noticed in each plot is due to the thermal cycle of the thermostatic cell between 24.6 and 25.4°C with a period of 40 minutes.

The temperature change influences the vapor tension of the substance modifying the moisture content in the headspace of the jar.

For the sensors designated to the packages have been used the following solutions: 92-97-100%.

The sensors have been placed inside the headspace of the jar, using a specific and modified cap.

4 sensors have been calibrated with specific software. The signal of each sensor (Volt output) has been recorded. For each sensor the values of voltage and time have been plotted (only the plot of the first sensor is reported for each salt solution)

Figure 3.32: signal of sensor # 1 (RH: 92%) – sampling 30 seconds.

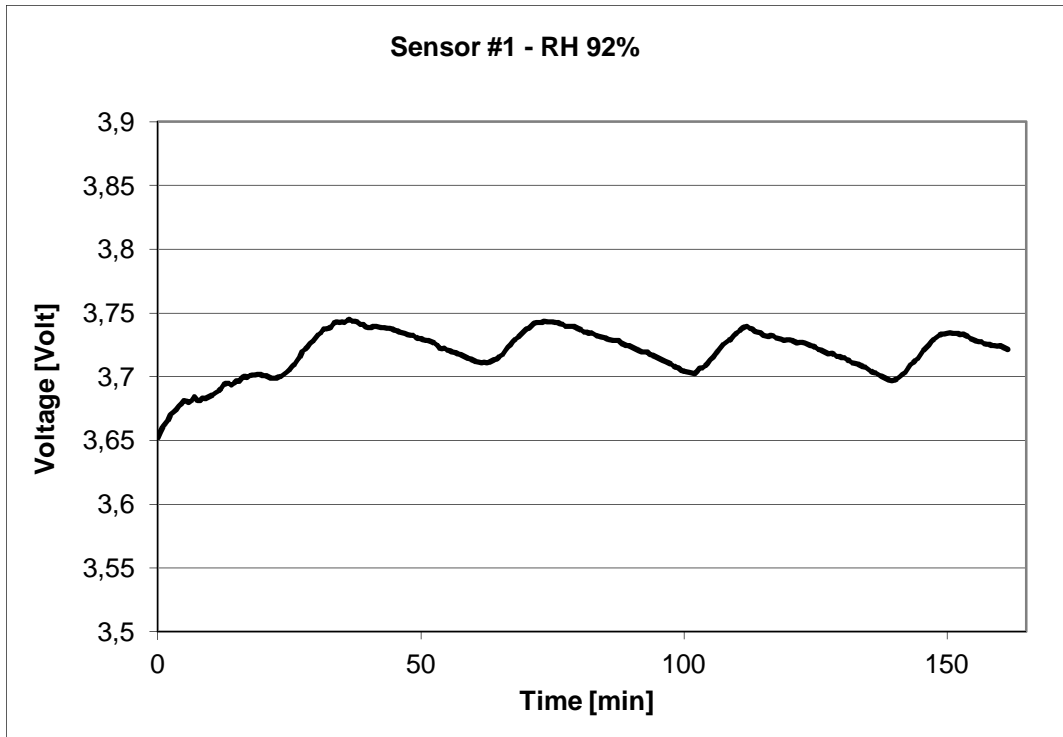


Figure 3.33: signal of sensor # 1 (RH: 97%) – sampling 30 seconds.

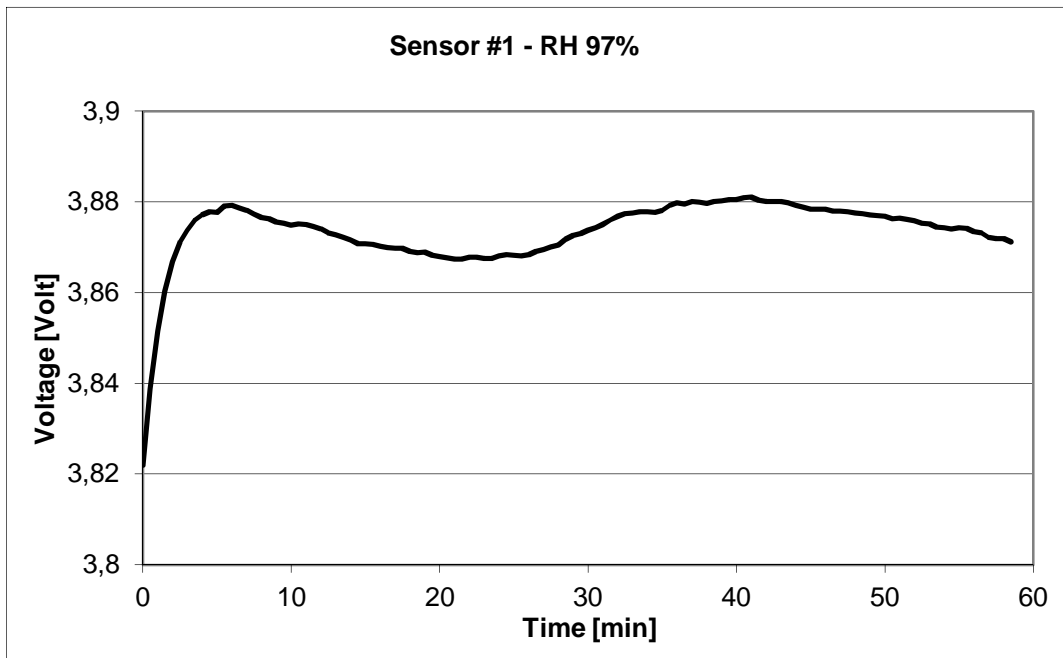
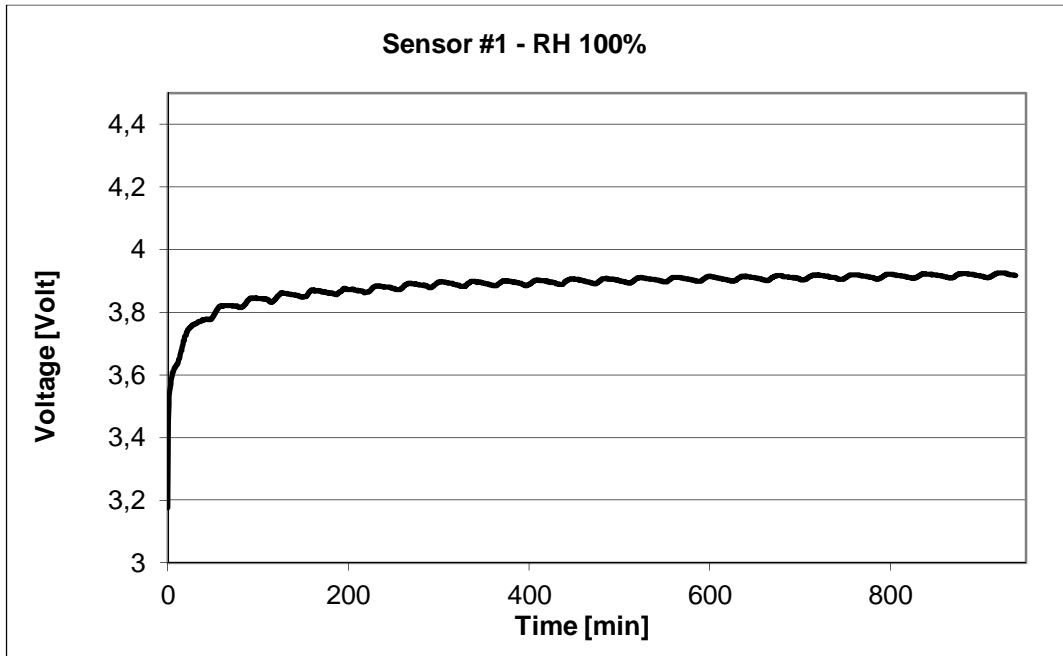


Figure 3.34: signal of sensor # 1 (RH: 100%) – sampling 30 seconds.



The values have been recorded with the specific software developed in collaboration with RDE Company. The sampling rate has been selected as the most appropriate for each signal on the basis of the specific characteristics of the output voltage of each sensor.

The scale of the voltage is different for each plot because the most appropriate scale to show the signal has been chosen in order to be sure to work at the steady state.

The scale of time is different for each plot because each saturated salt solution has a different equilibrium time. The attainment of the equilibrium before starting the calibration of the sensors is very important. The equilibrium time goes from 40 minutes to 12 hours, depending on the type of salt.

Experience shows that these differences in equilibrium time do not depend on the instrumentation but on the characteristics of the headspace inside each jar, specific for each salt solution.

The fluctuation that can be noticed in each plot is due to the thermal cycle of the thermostatic cell between 24.6 and 25.4°C with a period of 40 minutes.

The temperature change influences the vapor tension of the substance modifying the moisture content in the headspace of the jar.

The section of each plot that shows equilibrium between the solution and the headspace has been selected for each sensor and for each solution. The mean of voltage signal has been calculated for each sensor, shown in Table 3.8 and Table 3.9.

Table 3.8: mean output voltage for package sensors.

RH [%]	S1 [Volt]	S2 [Volt]	S3 [Volt]	S4 [Volt]	S5 [Volt]	S6 [Volt]	S7 [Volt]	S8 [Volt]
1.8	0.718816	0.719017368	0.719013158	0.719008316	0.718997632	0.718978263	0.718853737	0.718851
11	1.045402594	1.045404783	1.045404783	1.045404957	1.045408203	1.045410377	1.045405058	1.045397725
21.9	1.345308191	1.345311476	1.345312065	1.345313992	1.345318012	1.345321248	1.345315776	1.34530872
32.2	1.623418102	1.623418525	1.623418751	1.623419138	1.623419886	1.623420358	1.623419276	1.623417945
43.4	1.92932931	1.929329881	1.929330071	1.929330369	1.929331107	1.929331488	1.92933025	1.929328952
52.3	2.1845532	2.184555509	2.1845558	2.1845562	2.184556509	2.184557	2.184555782	2.1845544
80.2	3.022590179	3.022592692	3.022593256	3.022593692	3.022594385	3.022594564	3.022593462	3.022591231
RH [%]	S9 [Volt]	S10 [Volt]	S11 [Volt]	S12 [Volt]	S13 [Volt]	S14 [Volt]	S15 [Volt]	S16 [Volt]
1.8	0.718858579	0.718863474	0.718870737	0.718878474	0.718881895	0.718864684	0.718823526	0.718864421
11	1.045398	1.045399072	1.04539642	1.045397725	1.045399551	1.045400623	1.045402406	1.045402623
21.9	1.345309602	1.345308191	1.345304821	1.345305931	1.345307927	1.345308199	1.345308569	1.345308846
32.2	1.623417983	1.62341765	1.623416966	1.623417332	1.62341795	1.623418118	1.62341811	1.623418311
43.4	1.929329107	1.929328726	1.929328012	1.929328631	1.929329738	1.929329845	1.929329381	1.929329357
52.3	2.184554255	2.184553764	2.184552455	2.1845526	2.184553636	2.184553764	2.184553727	2.184553273
80.2	3.02259041	3.022589462	3.022588795	3.02258941	3.022590308	3.022591154	3.022590282	3.022589231

Table 3.9: mean output voltage for box sensors.

RH [%]	S1 [Volt]	S2 [Volt]	S3 [Volt]	S4 [Volt]
80.2	3.318915944	3.318916796	3.318933111	3.318932481
93.1	3.724968272	3.72497021	3.724985287	3.724983754
97.4	3.874623947	3.874625115	3.874640637	3.874637195
99.2	3.934676173	3.93468168	3.934697157	3.934693292

For each sensor all the points Voltage/Humidity have been considered, as reported in Figure 2.35 and 2.36 (only the plot of the first sensor of the package and the first of the boxes is reported).

Figure 3.35: signal of sensor # 1 – package.

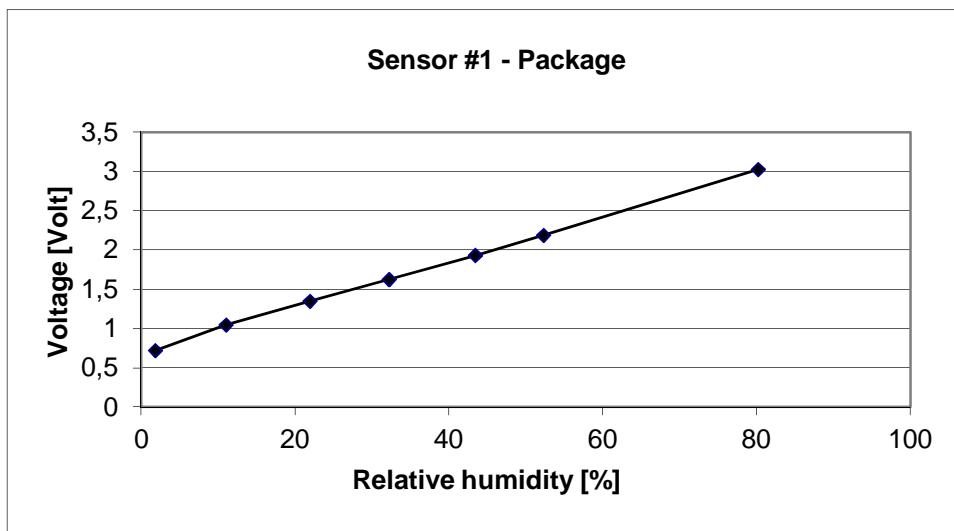
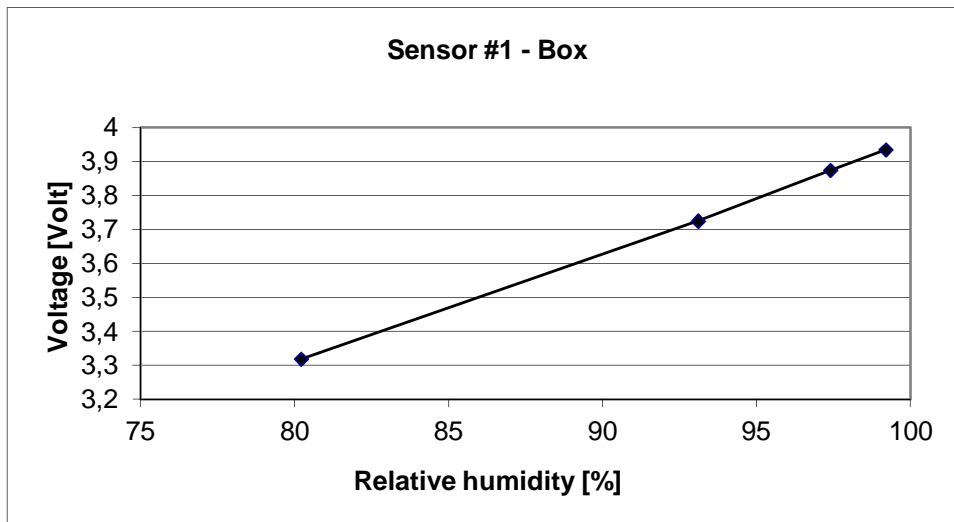


Figure 3.36: signal of sensor # 1 – boxes.



Experimental points have been interpolated. Coefficients m and q have been reported in Table 3.10 and 3.11.

Table 3.10: package sensors m and q coefficients.

Coefficient	S1	S2	S3	S4	S5	S6	S7	S8
m1	28.17017037	28.1873614	28.18699778	28.1865646	28.18536165	28.18350161	28.17321323	28.1736098
q1	-18.44916919	-18.46720242	-18.46682228	-18.46637434	-18.46520827	-18.46332504	-18.45241961	-18.45262758
m2	36.3447702	36.34463736	36.34456593	36.3443535	36.34425971	36.34413103	36.34414954	36.34411604
q2	-26.99491706	-26.99485772	-26.99478305	-26.9945673	-26.99458723	-26.99453172	-26.99435776	-26.99405621
m3	37.03571711	37.03609824	37.03614668	37.03635172	37.03678751	37.03715553	37.03657103	37.03580845
q3	-27.92445359	-27.92508797	-27.92517497	-27.92552218	-27.92625735	-27.92687229	-27.92588331	-27.92459605
m4	36.61193097	36.61191316	36.61191737	36.61192809	36.61192928	36.61194023	36.61195883	36.61195487
q4	-27.2364715	-27.23645805	-27.23647316	-27.23650473	-27.23653405	-27.23656912	-27.23655968	-27.23650453
m5	34.87134368	34.87110626	34.87109254	34.87107855	34.87113717	34.87112214	34.87111942	34.87113093
q5	-23.87830542	-23.8778673	-23.87784746	-23.87783085	-23.87796968	-23.87795398	-23.87790556	-23.8778825
m6	33.29208696	33.29207887	33.29206802	33.29206659	33.29205137	33.29206374	33.29205915	33.29209287
q6	-20.42833511	-20.42839431	-20.42838028	-20.42839048	-20.42836752	-20.42841089	-20.4283603	-20.42838797

Coefficient	S9	S10	S11	S12	S13	S14	S15	S16
m1	28.17423994	28.17456974	28.17542529	28.17598035	28.17611799	28.17454039	28.17083583	28.17434511
q1	-18.45329409	-18.45366907	-18.45448874	-18.45510575	-18.45530108	-18.45368208	-18.44985955	-18.45353429
m2	36.34404251	36.34434342	36.3444304	36.34445398	36.3444334	36.34453036	36.34470156	36.3446944
q2	-26.99398936	-26.9943429	-26.99433743	-26.99440949	-26.99445434	-26.99459468	-26.99483844	-26.99483887
m3	37.03592086	37.0357774	37.03541969	37.03551871	37.03570219	37.03571609	37.0357664	37.03577648
q3	-27.92477993	-27.9245347	-27.92392866	-27.92410297	-27.92442374	-27.92445252	-27.92453391	-27.92455769
m4	36.6119409	36.6119466	36.61195026	36.61191999	36.61186146	36.61186874	36.61192337	36.61195025
q4	-27.23648325	-27.2364803	-27.2364612	-27.23642547	-27.23635308	-27.23637105	-27.23645944	-27.23651043
m5	34.87117195	34.87118697	34.87126824	34.87133294	34.87134261	34.87133986	34.8712814	34.87134025
q5	-23.87796704	-23.87798274	-23.87811462	-23.87826105	-23.87831831	-23.87831674	-23.87818775	-23.87830047
m6	33.29211969	33.29213788	33.29211236	33.29209369	33.29209921	33.29207065	33.29210384	33.29212754
q6	-20.42844171	-20.4284651	-20.42836576	-20.42832982	-20.42837638	-20.42831823	-20.42838952	-20.42842618

Table 3.11: m and q coefficients.

Coefficient	S1	S2	S3	S4
m7	31.7693044	31.76921946	31.76931629	31.76938698
q7	-25.23965093	-25.23939608	-25.24023576	-25.24045036
m8	28.73262243	28.73277014	28.73268472	28.73305131
q8	-13.92810693	-13.92871282	-13.92882784	-13.93014934
m9	29.97390965	29.97174398	29.97176673	29.97197765
q9	-18.73762812	-18.72927198	-18.72982535	-18.7305394

Once the equations have been obtained for each interval for each sensor and for each solution they have been used in the software developed by RDE Company to obtain a calibration for each sensor in the considered relative humidity range.

3.3 References

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4. Results and discussion

An acquisition system has been developed and built in collaboration with RDE Company to study the phenomena of moisture diffusion in a packaged perishable food. The acquisition system allowed us to place moisture sensors inside packages to collect and record moisture values to analyze the moisture diffusion inside the headspace of the package and inside the product.

4.1. Preliminary experiment

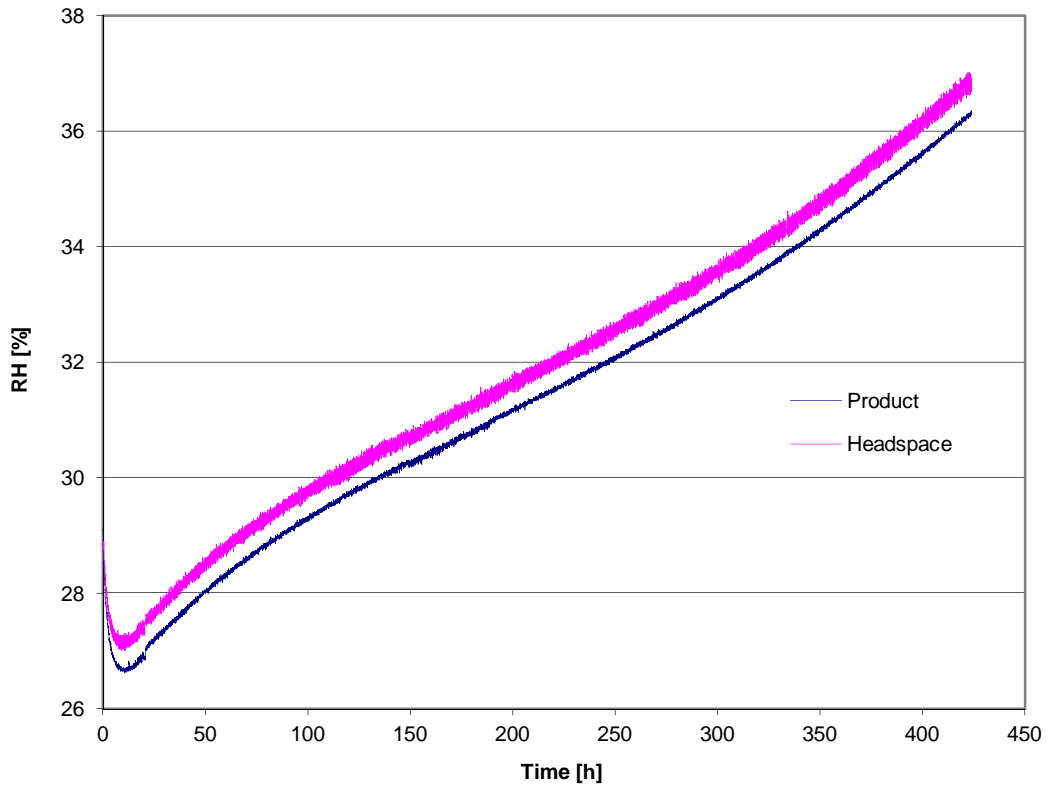
In a preliminary experiment 6 sliced air dried apple rings were sealed in packages of OPP 20 μm film. A moisture sensor was placed between the apple rings, another moisture sensor was placed in the headspace of the package (Figure 4.1).

Figure 4.1: apple rings package.



The packages have been placed in sealed plastic boxes. On the bottom of each box was present demineralized water to obtain a moisture content of 100% inside the box. The boxes were stored in a climatic chamber at 25°C and the system started to record moisture values. The moisture values collected are shown in Figure 4.2.

Figure 4.2: moisture change in an apple rings package.



The “Headspace” curve represents the moisture diffusion in the headspace, while the “Product” curve represents the moisture adsorption by the apple rings. The initial decrease of the two curves is due to the adsorption by the dried apple rings of the moisture present in the environmental air. This preliminary experiment shows that there is not an immediate equilibrium between the relative humidity in the headspace of the packaging (which changes with the entrance of water vapour from the outside) and the relative humidity of the product.

4.2. Model system and theoretical assumption verification

To investigate and analyze the preliminary results obtained with the dried apple rings a model system has been developed in order to repeat the experiments in the same conditions and to control the volume of the packages.

Rigid EPS trays with two different volumes were selected as packages: 1400 and 1030 cm³. They have been sealed with OPP 20 μm film.

As food product “Fetta biscottata”, a typical Italian bakery product has been chosen for the present work because of its regular shape and geometry and the uniformity among different packages. All the experiments have been performed using “Fetta biscottata” Sample 1 “Dorate” described in Materials and Methods. The acceptable maximum moisture content for the consumption has been set at a relative humidity of 40%.

The moisture content and the water activity have been determined for “Fetta biscottata”. The water activity was equal to 0.251 ± 0.003 and the moisture content to 3.71 ± 0.27 g/100g.

Two moisture sensors were placed inside “Fetta biscottata” (Figure 4.3) and two moisture sensor were placed in the headspace of the package (Figure 4.4).

Figure 4.3: sensors placed inside “Fetta biscottata”.

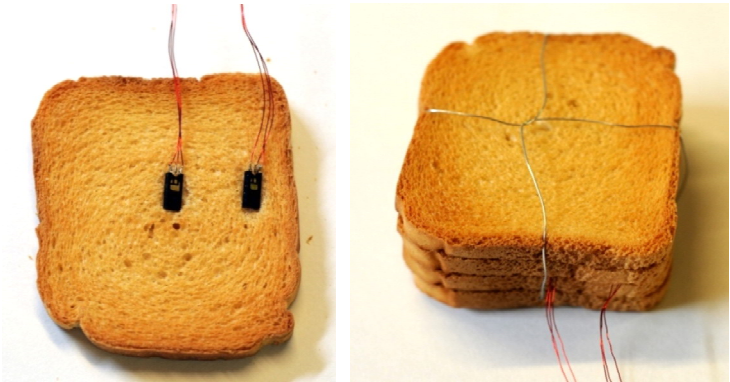
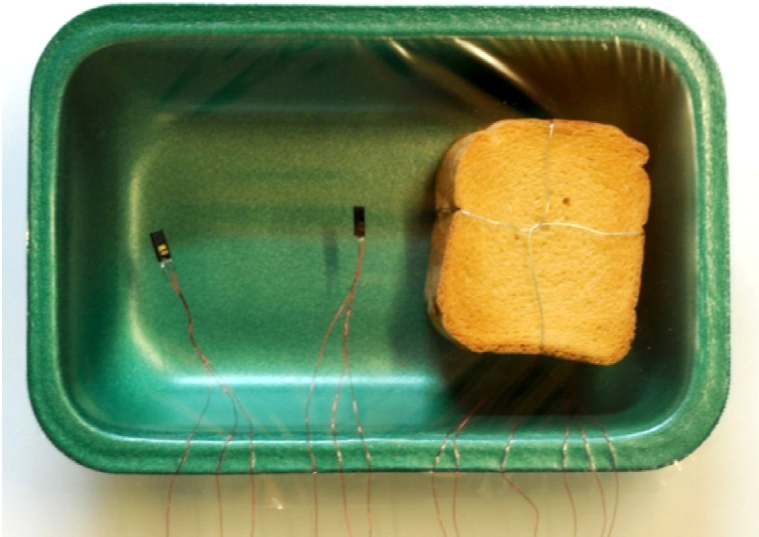


Figure 4.4: sensor placed in the headspace of the package.



Different quantities of the dry product (“Fetta biscottata”) have been packaged in the two types of trays, obtaining the combinations summarized in table 4.1.

Table 4.1: packaging combinations.

Sample number	Number of “Fetta biscottata”	Product weight [g]	Product volume [cm³]	Tray volume [cm³]	Headspace volume [cm³]
1	4	32.48	182.8	1030	847.2
2	4	32.48	182.8	1400	1217.2
3	6	48.72	274.2	1030	755.8
4	6	48.72	274.2	1400	1125.8
5	8	64.96	365.6	1030	664.4
6	12	97.44	548.4	1400	851.6

The packages have been placed in sealed plastic boxes. On the bottom of each box demineralized water was present to obtain a moisture content of 100% inside the box. The boxes were stored in a climatic chamber at 25°C and the system started to record moisture values.

During the storage the moisture adsorption by “Fetta biscottata” and the moisture increase in the headspace of the packages have been measured and recorded every 30 minutes for each combination. In Figure 4.5 and 4.6 the moisture changes for sample 2 and 6 are shown. The experiments were repeated at least two times for each sample.

Figure 4.5: moisture change in sample 2.

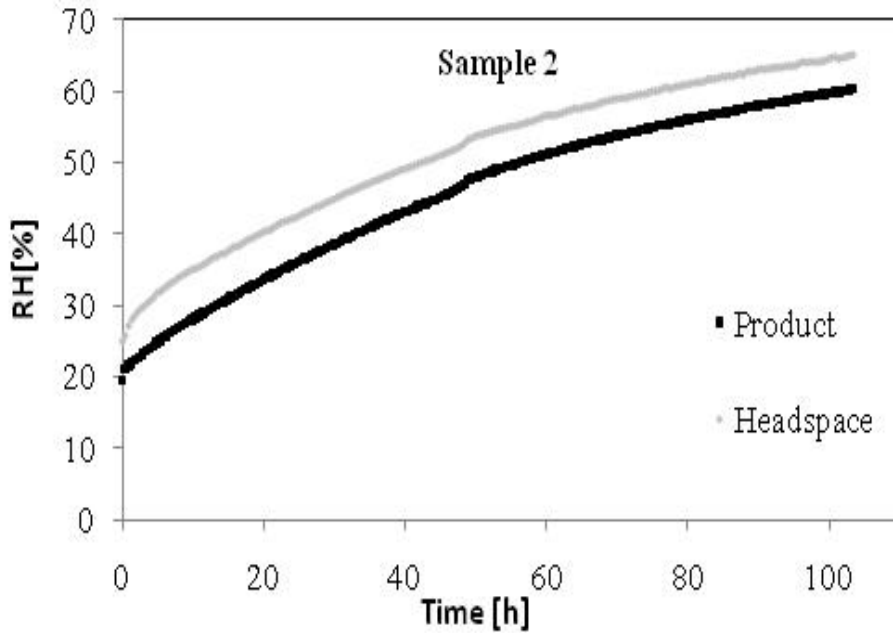
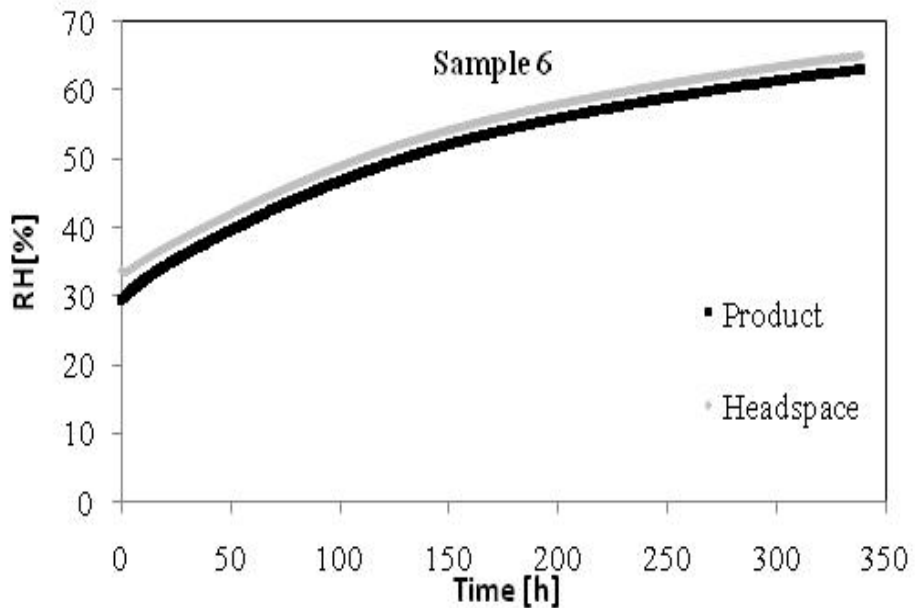


Figure 4.6: moisture change in sample 6.



The “Headspace” curve represents the moisture diffusion in the headspace, while the “Product” curve represents the moisture adsorption by “Fetta biscottata”.

In table 4.2 are reported the average RH differences between the “Headspace” curve and the “Product” curve for each sample.

Table 4.2: RH differences between the curves.

Sample number	$\Delta\% \text{ RH}$
1	4.5±0.6
2	5.6±1.5
3	2.9±0.5
4	3.6±0.6
5	2.5±0.3
6	2.2±0.3

For all the samples the difference between the curves can be considered constant in the considered RH range and it shows the delay of the products in adsorbing the moisture. Experiments conducted until 95% RH demonstrated that the two curves joint after a quite long time (data not shown).

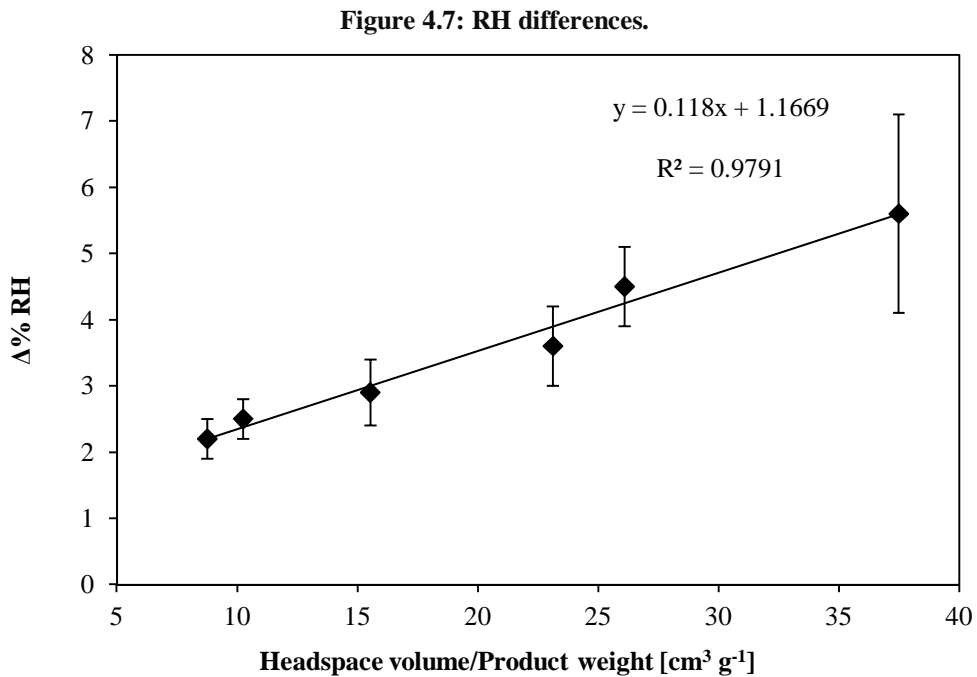
To analyze the differences among the samples, the ratio between the headspace volume and the product weight was related to the difference between the headspace and the product RH values. The results are reported in table 4.3.

Table 4.3: $\Delta\% \text{ RH}$ and Headspace volume/Product weight relation

Sample number	Headspace volume/Product weight [$\text{cm}^3 \text{ g}^{-1}$]	$\Delta\% \text{ RH}$
1	26.1	4.5±0.6
2	37.5	5.6±1.5
3	15.5	2.9±0.5
4	23.1	3.6±0.6
5	10.2	2.5±0.3
6	8.7	2.2±0.3

The data obtained show that the higher the ratios, the bigger the differences. This phenomenon is explained by the resistance of the stagnant air layer (Gennadios et al., 1994) inside the package, which is an obstacle to moisture diffusion.

In figure 4.7 the differences in RH values are plotted versus the volume/weight ratio.



The plot shows a linear relationship (in the considered range) between the ratio headspace volume/product weight and the headspace and product $\Delta\% RH$:

$$\Delta RH = 0.118 \times \frac{V_{\text{Headspace}}}{W_{\text{product}}} + 1.1669 \quad (4.1)$$

From our data, obtained combining different weights of “Fetta biscottata” and different headspace volumes, we can conclude that the relative humidity of the headspace of the packaging (which changes for the water vapour permeability) is not immediately in equilibrium with the product. The theoretical assumption generally used in the shelf life modeling (Quast & Karel, 1972; Bell & Labuza, 2000; Fava et al, 2000) has not been verified for this product.

4.3 Shelf life prediction

A shelf life prediction model has been applied to the product and the considered package to evaluate how the difference between the headspace and the product RH values influences the shelf life prediction. For this type of moisture sensitive products the prediction models are based on the water amount that permeates through the packaging film in a time unit. The water amount that permeates through the packaging film in a time unit is a function of the package characteristics (permeability coefficient of the material, KP ; thickness, L ; and area exposed to the mass flux, A) and of the driving force (Δp), according to the expression:

$$dQ = \frac{KP_{H_2O}}{L} \cdot A \cdot \Delta p \cdot dt \quad (4.2)$$

The driving force is represented by the product of the water vapour pressure (p_0) and the difference between the relative humidity inside and outside the package ($a_{w\ out} - a_{w\ in}$).

Temperature and water activity outside the package are considered to be constant, while $a_{w\ in}$ is subjected to continuous variation as a consequence of water absorption from the low-moisture product used in the model system. The modification of $a_{w\ in}$ is described by the adsorption isotherm of the considered product, so the driving force can be expressed as:

$$\Delta p = p_0 \cdot [a_{w\ out} - a_{w\ in} \cdot f(M)] \quad (4.3)$$

In case of hygroscopic products, such as the “Fetta biscottata” used in the present work, the water amount Q that permeates through the package film is absorbed by the product. The moisture content M can be expressed as:

$$M = \frac{Q}{W_s} \quad (4.4)$$

Where W_s is the total solids weight of the packaged product.

Hence, the general model that describes moisture content changes during time in this kind of products can be written as follows:

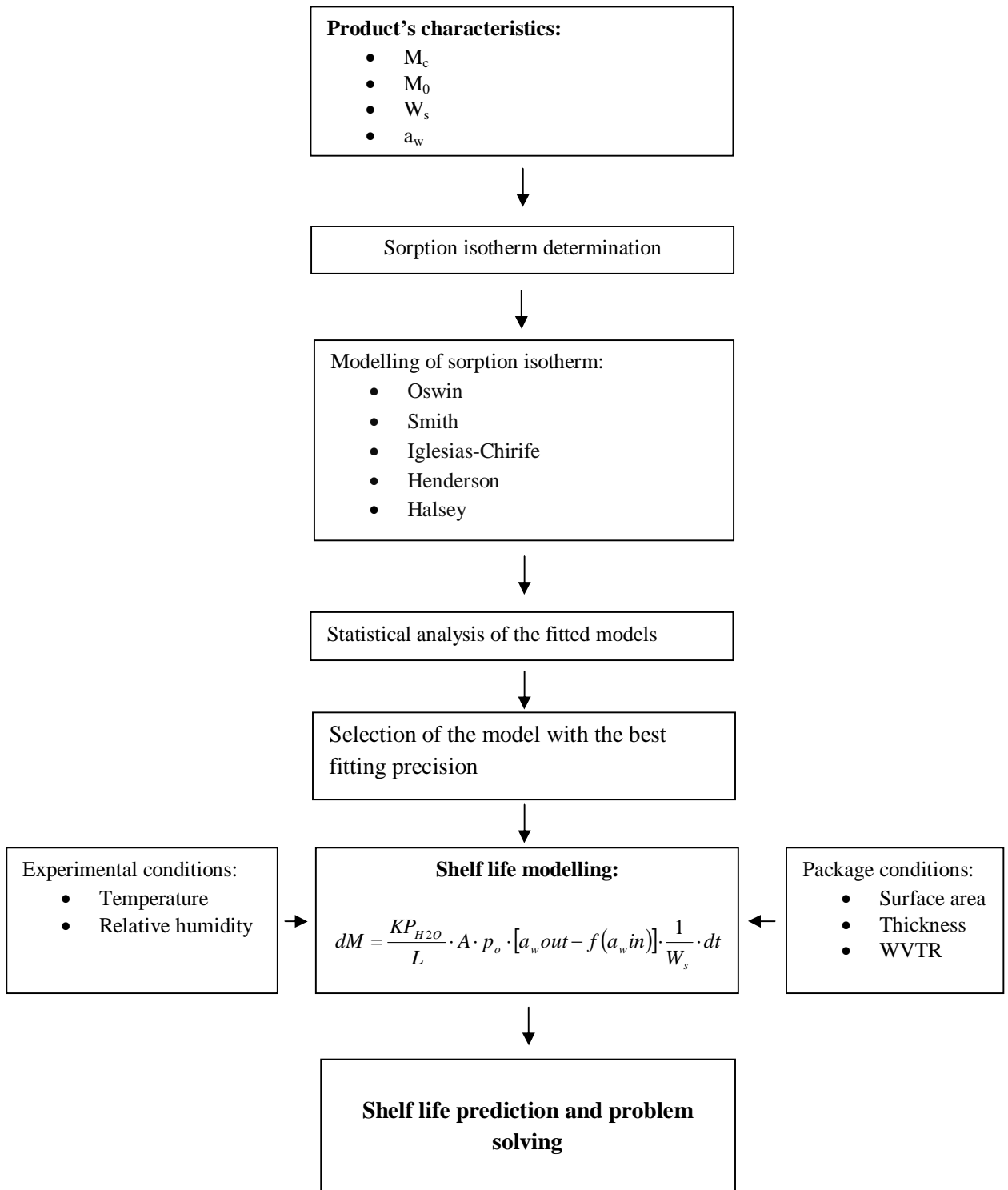
$$dM = \frac{KP_{H_2O}}{L} \cdot A \cdot p_o \cdot [a_{w\ out} - f(a_{w\ in})] \cdot \frac{1}{W_s} \cdot dt \quad (4.5)$$

In order to solve this differential equation, the following variables have to be known:

- absorption isotherm expressed as $a_w = f(M)$;
- initial moisture content M_0 , and the corresponding a_{w0} ;
- ratio A/W_s , related to the package geometric characteristics;
- water-barrier properties of the package film;
- storage conditions in terms of temperature and relative humidity.

Figure 4.8 is a schematic representation of the main variables to be introduced in the model for a shelf life study.

Figure 4.8: Flow-sheet of the main steps of a shelf life study.

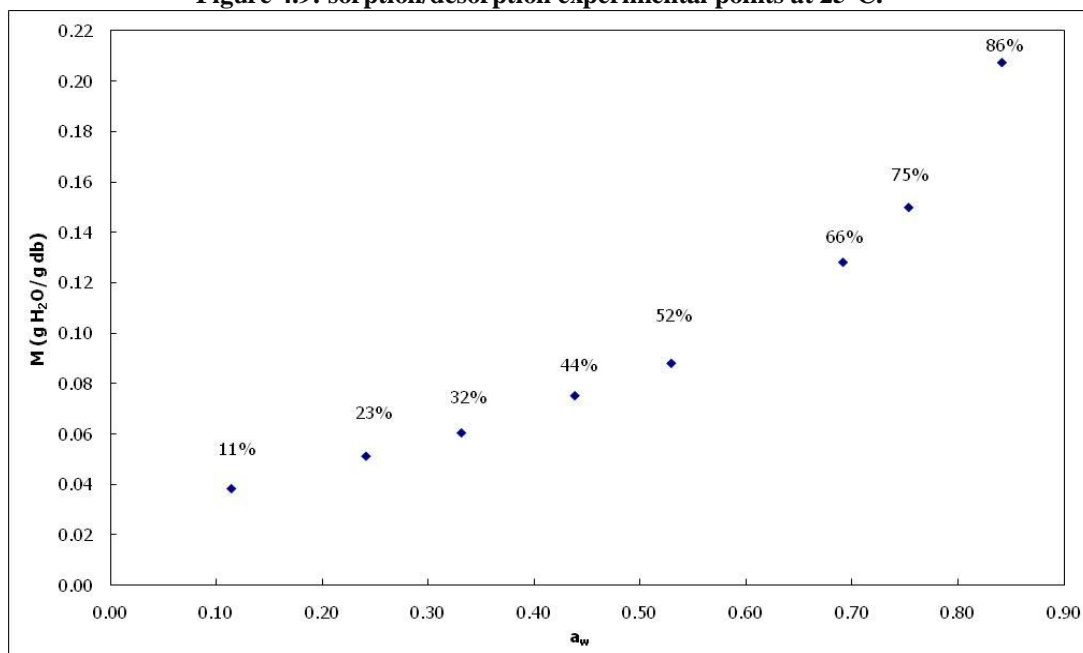


The water vapour sorption/desorption isotherm for “Fetta biscottata” was determined according to the static, gravimetric method developed by COST-90 Project (Wolf et al., 1985) and described by Bell and Labuza (2000). Based on the equilibrium moisture content at a given water activity, the sorption/desorption experimental points were obtained at 25°C (Table 4.4 and Figure 4.9).

Table 4.4: sorption/desorption experimental points at 25°C.

RH%	a_w	M (g H₂O/g db)
11	0.114	0.0381
23	0.241	0.051
32	0.331	0.0603
44	0.438	0.0751
52	0.529	0.0879
66	0.691	0.1281
75	0.753	0.1499
86	0.841	0.2076

Figure 4.9: sorption/desorption experimental points at 25°C.



The sorption/desorption curve at 25°C for “Fetta biscottata” was obtained fitting experimental data by the equations of Oswin (1946), Smith (1947), Iglesias-Chirife (1978), Henderson (1952) and Halsey (1948) using the Table Curve 2D software (Software output example for Oswin equation in Figure 4.10) obtaining the equation coefficients reported in table 4.5.

Figure 4.10: Table Curve 2D software output.

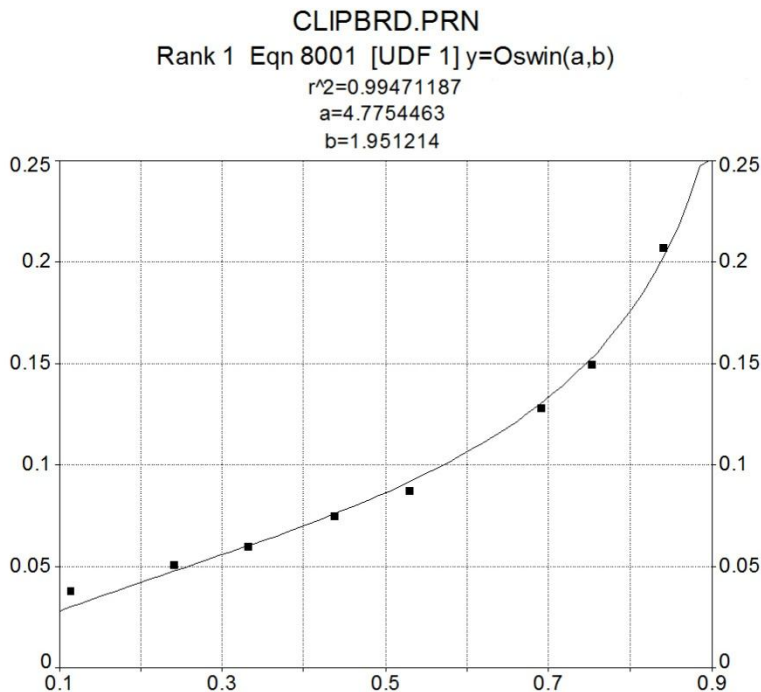


Table 4.5: equation coefficients.

Equation	a	b
Oswin	4.77544	1.95121
Smith	0.02134	0.09591
Iglesias-Chirife	0.03233	0.04552
Henderson	2.67036	1.26086
Halsey	0.14696	3.56937

In order to identify the equation that better fitted the experimental data, the correlation coefficient (r^2) and the mean relative percentage deviation modulus ($\bar{E}\%$) were considered, calculated with the formula:

$$\bar{E}\% = \frac{100}{N} \sum_{i=1}^N \frac{|M_e - M_p|}{M_e} \quad (4.6)$$

Where:

- N: number of experimental data;
- M_e : moisture content experimental value;
- M_p : moisture content predicted value.

The statistical parameters obtained for the different equations are listed in table 4.6.

Table 4.6: statistical parameters for the fitted equations.

Equation	r^2	$\bar{E}\%$
Oswin	0.995	4.826
Smith	0.992	5.258
Iglesias-Chirife	0.984	8.846
Henderson	0.978	11.163
Halsey	0.845	27.827

A $\bar{E}\%$ value below 10% indicates a reasonably good fit and values below 5% represent an extremely good fitting for practical purposes (Lomauro et al., 1985). According to r^2 and $\bar{E}\%$ values, the best fitting was obtained for the Oswin equation, as evidenced in table 4.6.

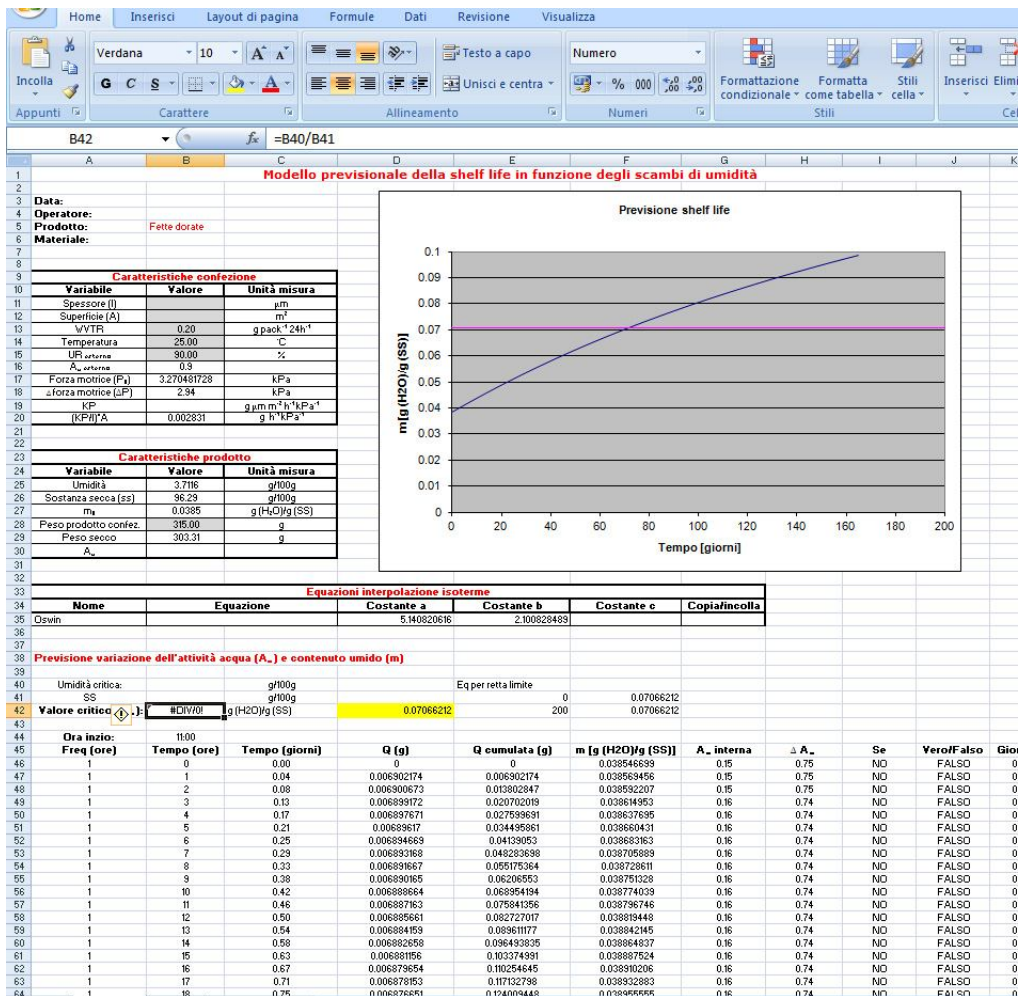
The statistical parameters calculated for the other equations showed that these equations did not provide a good fitting of the experimental data. Oswin equation was selected to interpolate the experimental points of the sorption/desorption isotherm.

In order to solve the differential equation, the model was implemented in a spreadsheet (Microsoft Office Excel 2007), in which all the variables related to the product (M , a_w , Weight), the package (KP, A, L) and the storage conditions (temperature, a_w), were included.

The Oswin equation was used in the spreadsheet to turn the moisture content value of the product into the corresponding water activity value. The water activity value is necessary to calculate the driving force as difference between the outside water activity and the product water activity. The constant a and b values, obtained from the Oswin equation describing the isotherm and expressed in

this section as $a_w=f(M)$, were also indicated. Figure 4.11 shows, as an example, the spreadsheet used for one of the samples.

Figure 4.11: spreadsheet used to predict the shelf life of one sample.



A time interval of one hour was assumed for the calculations, being considered appropriate for this kind of products. Within each time interval, the amount of water permeated into the package has been calculated as a function of the driving force (Δa_w) and the package characteristics. Water activity modification inside the package was calculated by means of the Oswin equation used for the isotherm, and a new driving force value was obtained for each time interval. The shelf life, expressed in hours, was determined at the reach of the critical moisture value set for "Fetta biscottata".

The values listed in table 4.7 report the shelf life predicted for each sample by the prediction model.

Table 4.7: shelf life prediction values.

Sample number	Predicted SL [h]
1	85
2	63
3	129
4	94
5	170
6	188

To evaluate the influence of the difference between the relative humidity of the headspace and the relative humidity of the product on the shelf life prediction the Microsoft Excel spreadsheet model has been modified applying the linear correlation previously described (Equation 4.1):

$$\Delta RH = 0.118 \times \frac{V_{\text{Headspace}}}{W_{\text{product}}} + 1.1669 \quad (4.1)$$

This correction allowed to consider the lower value of relative humidity described by equation 4.1 and the consequent delay of time to reach the critical moisture content, leading to a longer shelf life prediction for all the samples considered. The corrected values of shelf life are reported in table 4.8 in terms of hours and percentage error.

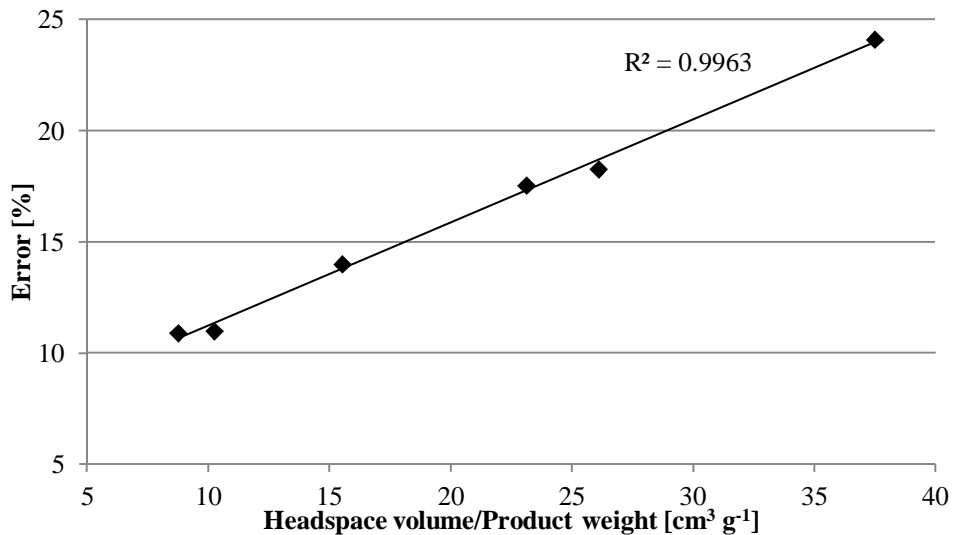
Table 4.8: shelf life prediction values.

Sample number	Predicted SL [h]	Headspace volume/Product weight [cm ³ g ⁻¹]	Corrected SL [h]	SL Error [h]	SL Error [%]
1	85	26.1	106	21	19.8
2	63	37.5	83	20	24.1
3	129	15.5	149	20	13.4
4	94	23.1	112	18	16.1
5	170	10.2	192	22	11.5
6	188	8.7	211	23	10.9

The application of equation 4.1 to the spreadsheet model allowed to correct the shelf life for every value of headspace volume/product weight ratio in the range considered during this trial, between 8.7 and 37.5 cm³ g⁻¹.

Figure 4.12 shows how, in the considered range, to the increase of the ratio headspace volume/product weight corresponds an increase of the percentage error on the shelf life prediction, following a linear relationship. The increase of the percentage error underlines the importance of the correction to the prediction model.

Figure 4.12: % error increase.



4.4 Conclusions

The model system studied in the present work has demonstrated that, in this case, the theoretical assumption generally used in the shelf life modelling, stating the immediate equilibrium between the headspace moisture and the product moisture, is not verified. These relative moistures are not immediately in equilibrium but show an increasing difference correlated to the increase of the headspace volume/product weight ratio. This correlation has been studied and it has been described by a linear equation in the studied range.

The application of a shelf life prediction model to the studied system has shown that a correction is needed to avoid an underestimation of the shelf life.

Further studies on other types of moisture sensitive products will be necessary to confirm the obtained results. The application of this correction will be particularly interesting for the shelf life modelling of moisture depending products characterized by packaging solutions with high headspace volumes.

4.5 Shelf life prediction simplification for a category of products

In a second part of the work the possibility to simplify the shelf life prediction for a category of products has been studied, applying a unique shelf life model for all the products part of the category.

14 different types and brands of “Fetta biscottata” have been bought in different supermarkets in the city of Milano without any specific criteria, just on the base of the availability.

For all of them the water activity and the moisture content have been determined, as reported in Table 4.9.

Table 4.9: water activity and moisture content for “Fetta biscottata”.

Sample	a_w	Moisture content [g/100g]
1	0.251±0.003	3.71±0.27
2	0.307±0.003	4.86±0.04
3	0.198±0.003	3.28±0.07
4	0.183±0.005	3.25±0.13
5	0.185±0.005	3.41±0.04
6	0.232±0.003	3.08±0.11
7	0.292±0.006	5.63±0.22
8	0.307±0.003	5.08±0.14
9	0.282±0.009	3.69±0.08
10	0.206±0.013	3.15±0.14
11	0.185±0.007	2.85±0.04
12	0.163±0.006	2.9±0.1
13	0.149±0.004	2.82±0.07
14	0.187±0.002	3.44±0.08

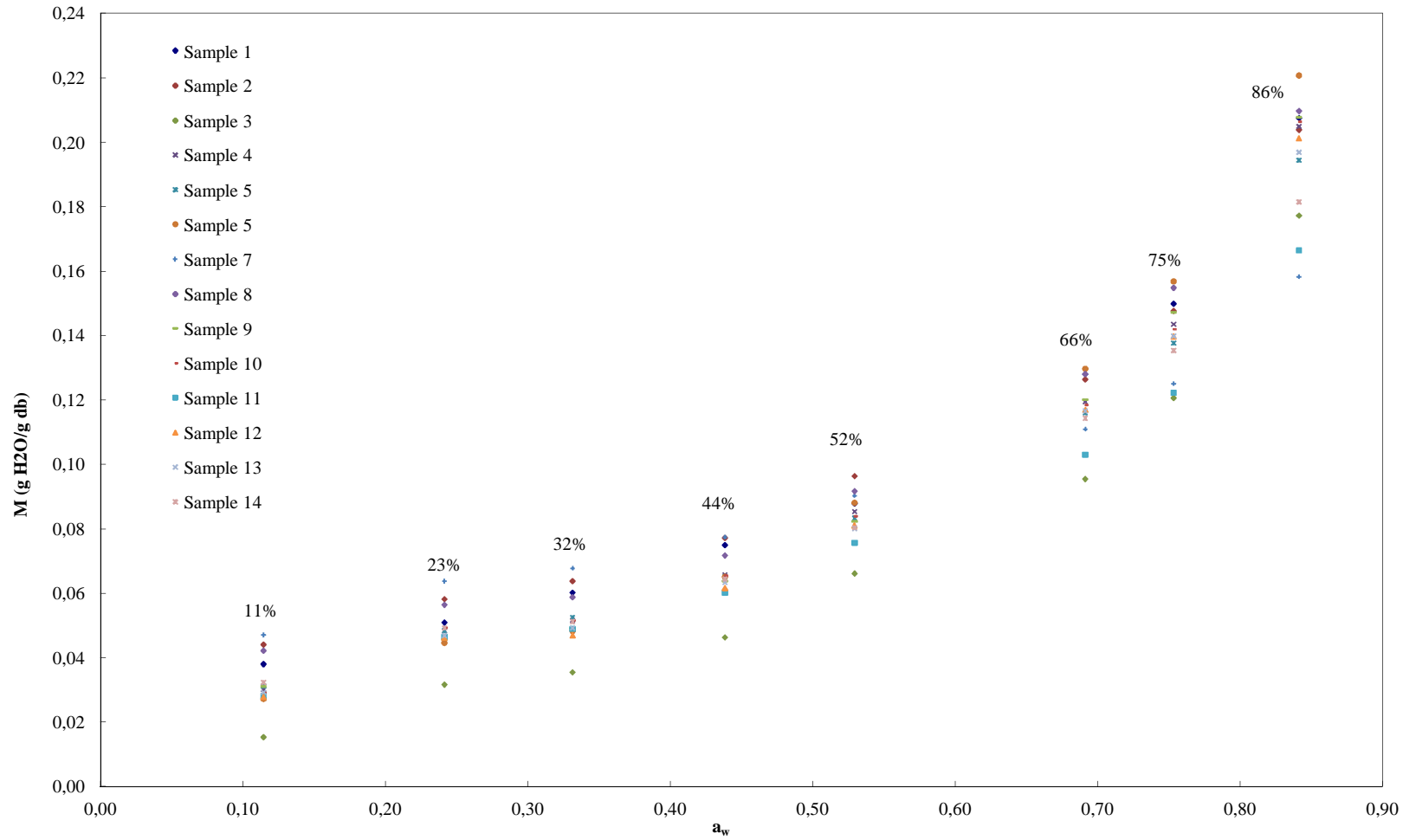
The water vapour sorption/desorption isotherm for “Fetta biscottata” was determined according to the static, gravimetric method developed by COST-90 Project (Wolf et al., 1985) and described by Bell and Labuza (2000). Based on the equilibrium moisture content at a given water activity, the sorption/desorption experimental points were obtained at 25°C (Table 4.10 and Figure 4.13).

Table 4.10: sorption/desorption experimental points at 25°C.

RH%	a_w	M (g H₂O/g db) Sample 1	M (g H₂O/g db) Sample 2	M (g H₂O/g db) Sample 3	M (g H₂O/g db) Sample 4	M (g H₂O/g db) Sample 5	M (g H₂O/g db) Sample 6	M (g H₂O/g db) Sample 7
11	0.114	0.0381	0.0441	0.0154	0.0302	0.0313	0.0273	0.0472
23	0.241	0.0510	0.0583	0.0317	0.0484	0.0485	0.0447	0.0639
32	0.331	0.0603	0.0639	0.0356	0.0517	0.0526	0.0484	0.0679
44	0.438	0.0751	0.0773	0.0464	0.0658	0.0653	0.0652	0.0775
52	0.529	0.0879	0.0964	0.0662	0.0854	0.0835	0.0882	0.0904
66	0.691	0.1281	0.1265	0.0955	0.1196	0.1161	0.1298	0.1111
75	0.753	0.1499	0.1477	0.1208	0.1436	0.1378	0.1569	0.1252
86	0.841	0.2076	0.2039	0.1773	0.2050	0.1945	0.2208	0.1584

RH%	a_w	M (g H₂O/g db) Sample 8	M (g H₂O/g db) Sample 9	M (g H₂O/g db) Sample 10	M (g H₂O/g db) Sample 11	M (g H₂O/g db) Sample 12	M (g H₂O/g db) Sample 13	M (g H₂O/g db) Sample 14
11	0.116	0.0422	0.0312	0.0292	0.0282	0.0279	0.0293	0.0324
23	0.205	0.0565	0.0458	0.0495	0.0466	0.0463	0.0470	0.0494
32	0.326	0.0589	0.0492	0.0517	0.0490	0.0471	0.0493	0.0513
44	0.443	0.0718	0.0639	0.0655	0.0603	0.0617	0.0635	0.0645
52	0.497	0.0918	0.0824	0.0840	0.0758	0.0811	0.0802	0.0805
66	0.65	0.1282	0.1202	0.1185	0.1031	0.1170	0.1167	0.1144
75	0.748	0.1549	0.1473	0.1421	0.1223	0.1398	0.1399	0.1354
86	0.816	0.2098	0.2078	0.2064	0.1665	0.2013	0.1970	0.1816

Figure 4.13: sorption/desorption experimental points at 25°C.



The sorption/desorption curve at 25°C for each sample of “Fetta biscottata” was obtained fitting experimental data by the equation of Oswin (1946), using the Table Curve 2D software, obtaining the equation coefficients reported in Table 4.11.

Table 4.11: equation coefficients.

Sample	a	b
1	4.77545	1.95121
2	5.16770	2.15641
3	4.28550	1.50597
4	4.54424	1.79117
5	4.78319	1.87670
6	4.17041	1.65331
7	7.20962	2.96054
8	4.79163	1.97556
9	4.39556	1.72048
10	4.51068	1.77215
11	5.31687	2.01470
12	4.46408	1.72491
13	4.60038	1.78719
14	5.06558	1.97900

In order to analyze for each type of “Fetta biscottata” the fitting properties of the Oswin equation for the experimental data, the correlation coefficient (r^2) and the mean relative percentage deviation modulus ($\bar{E}\%$) were considered, calculated with the Equation 4.6. The statistical parameters obtained for each type of “Fetta biscottata” are listed in table 4.12.

Table 4.12: statistical parameters.

Sample	r^2	$\bar{E}\%$
1	0.995	4.826
2	0.989	5.972
3	0.997	4.619
4	0.994	6.007
5	0.994	5.582
6	0.997	5.409
7	0.991	3.601
8	0.989	7.524
9	0.995	6.733
10	0.993	6.181
11	0.995	4.521
12	0.994	6.731
13	0.995	6.005
14	0.994	5.848

For all the considered samples the Oswin equation provided a reasonably good fit ($\bar{E}\%$ value below 10%) and for samples 1, 3, 7, and 11 extremely good fitting properties ($\bar{E}\%$ value below 5%).

A shelf life prediction model was implemented for each sample, using a spreadsheet (Microsoft Office Excel 2007), in which all the variables related to the product (M , a_w , Weight), the package (KP, A, L) and the storage conditions (temperature, a_w), were included. Moisture content and water activity were the ones that had been determined for each sample, as well as the sorption/desorption curve, while the package characteristics and the storage conditions were the same for every sample, in order to compare the obtained results.

In table 4.13 is reported the shelf life of each sample, expressed in hours.

Table 4.13: shelf life prediction.

Sample	SL [h]
1	71
2	45
3	27
4	67
5	64
6	69
7	38
8	41
9	55
10	69
11	64
12	68
13	71
14	61

This approach for predicting the shelf life of the samples required the application of 14 different prediction models, one for each sample.

In order to simplify the prediction and to reduce the necessary work, the possibility to apply a single sorption/desorption curve at 25°C for all the experimental points determined for the 14 samples and then apply a single prediction model has been considered.

The interpolation of the experimental points was obtained fitting experimental data by the equation of Oswin (1946), using the Table Curve 2D software (Figure 4.14) obtaining the equation coefficients reported in Table 4.14.

Figure 4.14: Table Curve 2D software output.

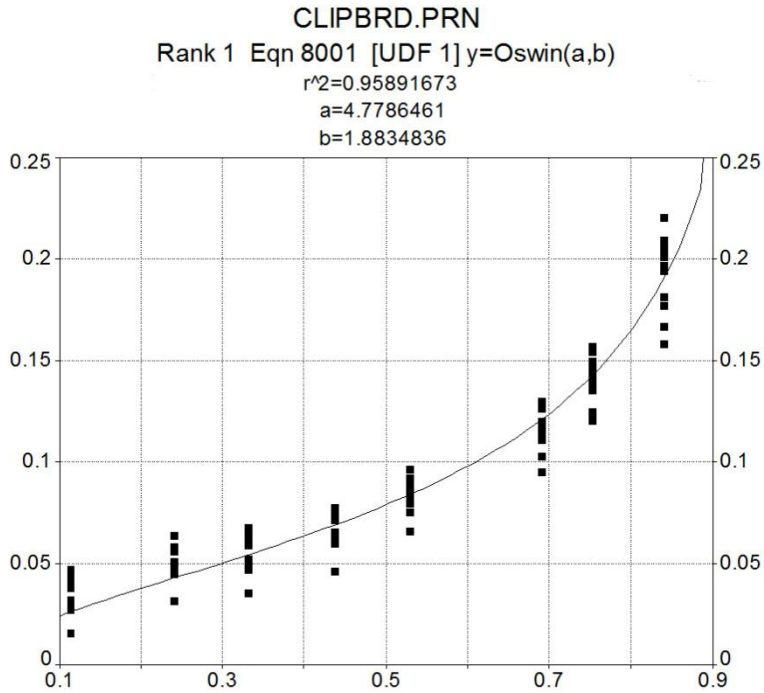


Table 4.14: equation coefficients

a	B
4.77865	1.88348

The correlation coefficient (r^2) and the mean relative percentage deviation modulus ($\bar{E}\%$), calculated with the Equation 4.6 show that this approach does not give good fitting properties. The statistical parameters obtained are listed in table 4.15.

Table 4.15: statistical parameters.

r^2	$\bar{E}\%$
0.959	11.331

The application of a unique shelf life prediction model was implemented using a single sorption/desorption curve for each of the samples, the same storage conditions and the same

package characteristics. Only the moisture content and water activity were the ones that had been determined for each sample. In table 4.16 is reported the shelf life of each sample, expressed in hours. The predicted shelf life obtained with this unique prediction model has been compared with the ones obtained with a specific prediction model and the errors have been calculated.

Table 4.16: shelf life prediction and error.

Sample	SL [h]	Predicted SL [h]	Error [h]	Error [%]
1	71	58	-13	18%
2	45	32	-13	29%
3	27	67	40	148%
4	67	68	1	1%
5	64	65	1	2%
6	69	71	2	3%
7	38	11	-27	71%
8	41	26	-15	37%
9	55	59	4	7%
10	69	70	1	1%
11	64	78	14	22%
12	68	75	7	10%
13	71	77	6	8%
14	61	64	3	5%

The results confirmed the indications obtained by the correlation coefficient and the mean relative percentage deviation modulus of Table 4.15. The errors in the shelf life prediction are unacceptable, especially for samples 3, 7, and 8.

The same approach has been applied excluding the sample number 3 with the highest error value.

The experimental points of the 13 samples were interpolated with the equation of Oswin (1946), using the Table Curve 2D software (Figure 4.15) obtaining the equation coefficients reported in Table 4.17 and the statistical parameters listed in table 4.18.

Figure 4.15: Table Curve 2D software output.

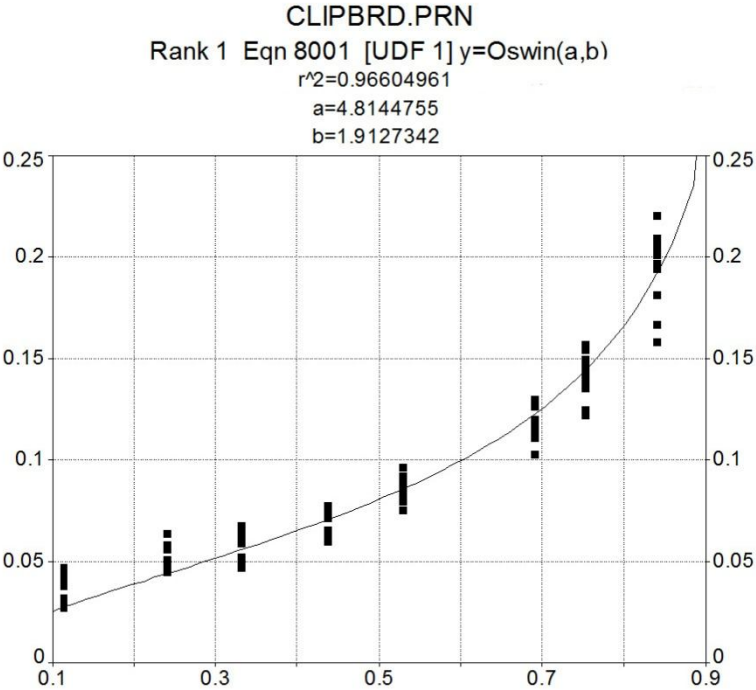


Table 4.17: equation coefficients

a	b
4.81448	1.91273

Table 4.18: statistical parameters.

r^2	$\bar{E}\%$
0.966	10.119

The correlation coefficient and the mean relative percentage deviation modulus show better fitting characteristics than before, but still over 10%. These results are confirmed by the application of the

shelf life model, the errors are lower than before but still too high, especially for sample 7, as reported in table 4.19.

Table 4.19: shelf life prediction and error.

Sample	SL [h]	Predicted SL [h]	Error [h]	Error [%]
1	71	61	-10	14%
2	45	35	-10	22%
3	27	-	-	-
4	67	70	3	4%
5	64	68	4	6%
6	69	74	5	7%
7	38	15	-23	61%
8	41	30	-11	27%
9	55	64	9	16%
10	69	73	4	6%
11	64	79	15	23%
12	68	78	10	15%
13	71	79	8	11%
14	61	67	6	10%

With the exclusion of sample 7 the interpolation of the experimental points of the 12 samples with the equation of Oswin (1946), using the Table Curve 2D software (Figure 4.16) returned the equation coefficients reported in Table 4.20 and the statistical parameters listed in Table 4.21.

Figure 4.16: Table Curve 2D software output.

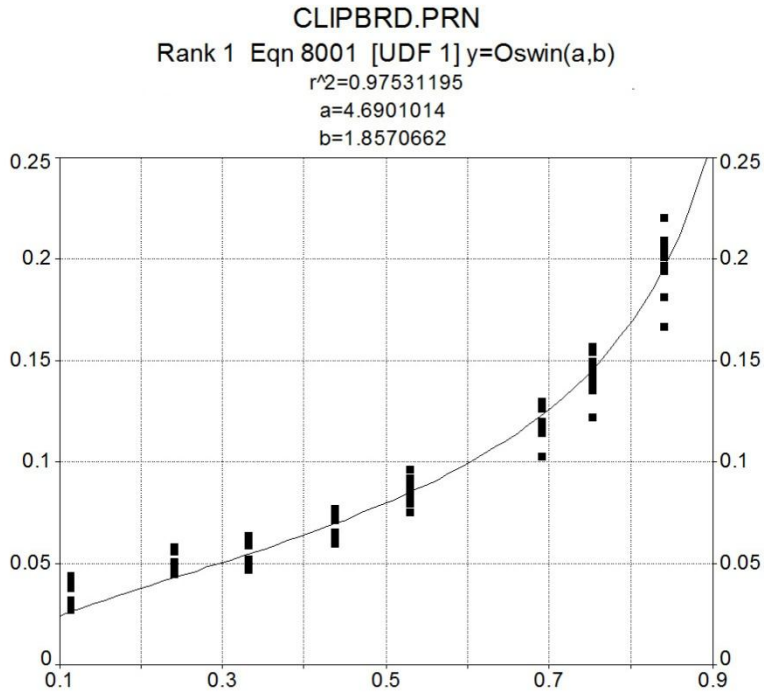


Table 4.20: equation coefficients.

a	b
4.69010	1.85707

Table 4.21: statistical parameters.

r^2	$\bar{E}\%$
0.975	8.667

The correlation coefficient and the mean relative percentage deviation modulus show good fitting characteristics. These results are confirmed by the application of the shelf life model as shown in Table 4.22. The errors are lower than 20% for each sample, a value that can be considered acceptable in this type of shelf life prediction.

Table 4.22: shelf life prediction and error.

Sample	SL [h]	Predicted SL [h]	Error [h]	Error [%]
1	71	59	-12	17%
2	45	37	-8	18%
3	27	-	-	-
4	67	69	2	3%
5	64	66	2	3%
6	69	72	3	4%
7	38	-	-	-
8	41	34	-7	17%
9	55	60	5	9%
10	69	71	2	3%
11	64	76	12	19%
12	68	76	8	12%
13	71	78	7	10%
14	61	65	4	7%

4.6 Conclusions

To predict the shelf life of moisture sensitive products it is necessary to determine the water activity and the moisture content of the considered products. It is also important to determine the sorption/desorption isotherm at the storage temperature to obtain a reliable shelf life prediction. This type of work is labor and time intensive. It is possible to simplify the work only with simplifications based on a good knowledge of statistical indexes and their correct application.

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5 Appendix

Verifica di modelli per la previsione della shelf life di prodotti secchi confezionati attraverso l'utilizzo di sensori di umidità relativa

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Introduzione

L'affidabilità di un modello di previsione della shelf life di prodotti alimentari secchi confezionati, in cui si considerano congiuntamente le variabili del sistema "prodotto/confezione/ambiente", si fonda sull'accuratezza con cui queste variabili sono misurate e sulla conoscenza delle relazioni che tra esse intercorrono (1). In particolare, deve essere attentamente valutato il ruolo svolto nel sistema dal prodotto alimentare. Diventa essenziale conoscere l'entità dell'interazione alimento/fattore di degradazione ed anche la relazione matematica che la descrive. Nel caso di prodotti che, per il ridotto tenore di umidità ed il basso valore di a_w , tendono ad assorbire velocemente vapor d'acqua dall'ambiente circostante, la relazione che descrive l'interazione alimento/fattore di degradazione è l'isoterma di adsorbimento del vapor d'acqua. Per giungere alla previsione della shelf life, questa relazione viene, di norma, inserita in un modello più generale che tiene conto della permeabilità al vapor d'acqua della confezione e dei valori di umidità del prodotto, iniziali e finali, cioè critici per l'accettabilità (2).

Sebbene, in molte applicazioni, tali modelli si siano mostrati attendibili, spesso si basano su assunzioni teoriche che non sono state ancora verificate sperimentalmente e che potrebbero indurre errori nella stima previsionale. Una di queste assunzioni si basa sull'ipotesi che l'umidità relativa del microambiente interno alla confezione (che si modifica per l'ingresso di vapore acqueo dall'esterno) sia immediatamente e sempre in equilibrio con quella del prodotto (3).

Scopo

Scopo del presente lavoro è quello di verificare le assunzioni teoriche alla base dei modelli previsionali mediante l'utilizzo di sensori di umidità relativa che, posti all'interno di confezioni contenenti rondelle di mele disidratate e fette biscottate, sono in grado di monitorare in continuo ed in modo puntuale le variazioni di umidità all'interno del prodotto e nello spazio di testa delle confezioni.

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Materiali e metodi

Rondelle di mela: sono state utilizzate mele biologiche (cv 'Golden delicious') private del torsolo tramite un detorsolatore del diametro di 25 mm, tagliate meccanicamente in rondelle dello spessore di $5,0 \pm 0,2$ mm e quindi disidratate in corrente d'aria a 80°C in un essiccatore ad armadio.

Fette biscottate: sono state utilizzate fette biscottate dorate, prodotte da Mulino Bianco (Barilla), acquistate presso la GDO.

Sistema di acquisizione: (Figura 1) per l'acquisizione dei valori di umidità relativa e per la taratura dei sensori è stato utilizzato un sistema di acquisizione dati fornito dalla società RDE Company srl (Novate Milanese, Milano).

Film plastico: film trasparente di OPP 20 (polipropilene orientato, spessore 20 μm) prodotto dalla Moplefan.

Vaschette: vaschette in polistirene rivestite con un film a barriera totale, prodotte da Sirap Gema.

Prove di conservazione simulata: Le prove di conservazione simulata sono state effettuate in celle termostate FOC 225 a $25 \pm 0,5^{\circ}\text{C}$ per le rondelle di mela e a $38 \pm 0,5^{\circ}\text{C}$ per le fette biscottate. Sul fondo delle vaschette di polipropilene è stata posizionata acqua demineralizzata, in quantità di circa 1 litro, in modo da ottenere una umidità relativa interna del 98%.

Risultati e discussione

Per verificarle le ipotesi teoriche alla base dei modelli previsionali sono state preliminarmente confezionate delle buste in OPP 20, contenenti 6 rondelle di mela disidratate ciascuna, in cui è stata inserita una coppia di sensori di umidità, uno dei quali direttamente a contatto con il prodotto e l'altro all'interno del microambiente non a diretto contatto.

In figura 2 è possibile osservare l'andamento dell'umidità in funzione del tempo. Vi è una iniziale riduzione del valore di umidità dovuto all'assorbimento, da parte del prodotto, dell'umidità presente nell'ambiente al momento della saldatura della confezione. Tale ritardo non è dovuto al tempo di permeazione dell'umidità attraverso il film, perché un'apposita prova, eseguita alle stesse condizioni sperimentali ma con confezioni vuote, ha evidenziato un immediato aumento di umidità all'interno delle confezioni sotto effetto della forza motrice.

Queste prove preliminari hanno mostrato una differenza di circa 0,5% di umidità relativa tra l'interno del prodotto e lo spazio di testa della confezione. Hanno però anche limiti dovuti al tipo di prodotto utilizzato: le rondelle di mela essiccate non sono mai perfettamente piane impedendo così di posizionare i sensori in maniera corretta; inoltre, essendo materiale vegetale, non garantiscono l'omogeneità, la riproducibilità e la ripetibilità necessaria ad effettuare un numero congruo di repliche.

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Per ovviare a queste problematiche si è deciso di utilizzare un prodotto più omogeneo e costante, quali le fette biscottate. Inoltre, al fine di poter conoscere con esattezza il volume dello spazio libero della confezione, sono state utilizzate vaschette rigide a barriera totale chiuse con un film OPP 20.

Per ciascuna confezione sono stati posizionati due sensori tra 4 fette biscottate e due sensori nello spazio libero.

In figura 3 è possibile osservare le media (con le relative incertezze) dell'andamento dell'umidità relativa umidità all'interno del prodotto e nello spazio libero di testa delle repliche effettuate .

La differenza tra le umidità relative è, in media, pari al $5,55 \pm 1,33\%$.

Conclusioni

Dai preliminari dati sperimentali si è notata una differenza di umidità all'interno delle confezioni: per le fette biscottate il valore di umidità relativa dello spazio libero della confezione è, in media, superiore dello $5,55 \pm 1,33\%$ rispetto al valore di umidità relativa misurato nell'ambiente a stretto contatto con l'alimento; pertanto l'ipotesi che l'umidità relativa del microambiente interno alla confezione sia immediatamente in equilibrio con quella del prodotto si è rivelata non corretta.

I risultati preliminari ottenuti mediante la sperimentazione hanno evidenziato che è necessario migliorare la catena di misura ed effettuare nuove prove in modo da avere un numero congruo di dati per una miglior comprensione dei fenomeni oggetto della sperimentazione e confrontarli con i modelli previsionali.

Prospettive future:

- utilizzare i dati rilevati dai sensori per ottimizzare e affinare i modelli previsionali;
- trasferire le conoscenze fin qui acquisite sulla parte sensoristica a tecnologie di trasmissione in radio frequenza, al fine di poter avere un semplice e valido ausilio per una stima corretta della conservabilità del prodotto e dei suoi reali livelli di qualità, aprendo interessanti prospettive di impiego e ulteriori campi di indagine e di approfondimento.

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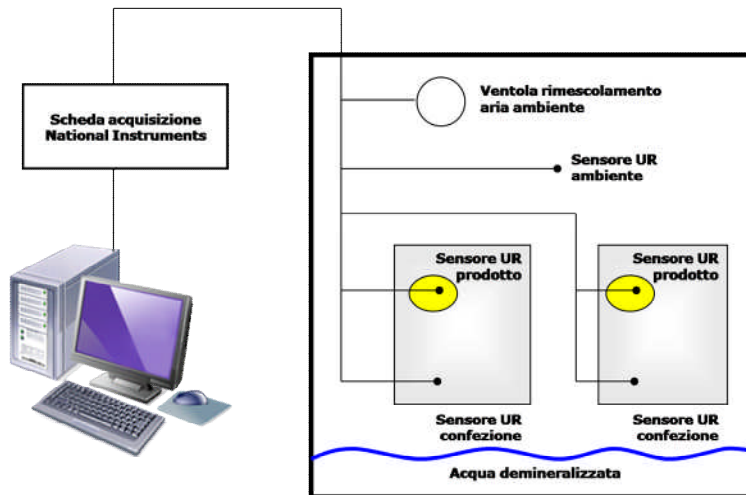


Figura 1: schema del sistema di acquisizione

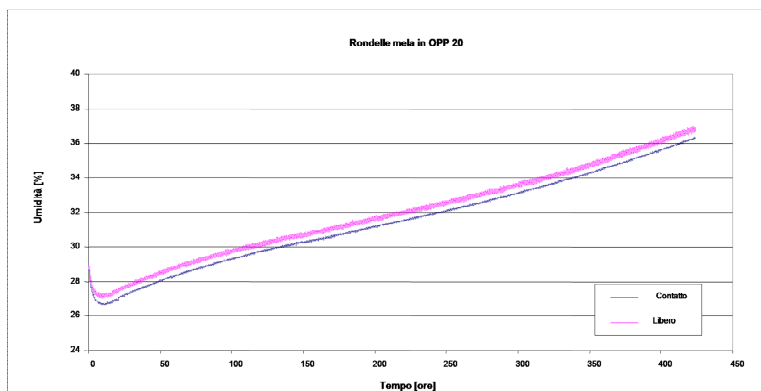


Figura 2: andamento dell'umidità relativa nelle confezioni di rondelle

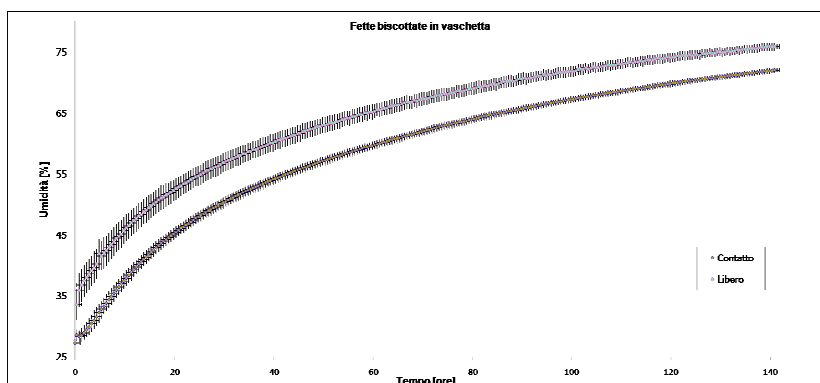


Figura 3: : andamento dell'umidità relativa nelle confezioni di fette biscottate

Riassunti

Verifica di modelli per la previsione della shelf life di prodotti secchi confezionati attraverso l'utilizzo di sensori di umidità relativa

L'affidabilità di un modello di previsione della shelf life di prodotti alimentari secchi confezionati, in cui si considerano congiuntamente le variabili del sistema "prodotto/confezione/ambiente", si fonda sull'accuratezza con cui queste variabili sono misurate e sulla conoscenza delle relazioni che tra esse intercorrono. Sebbene, in molte applicazioni, tali modelli si siano mostrati attendibili, spesso si basano su assunzioni teoriche che non sono state ancora verificate sperimentalmente e che potrebbero indurre errori nella stima previsionale. Una di queste assunzioni, ad esempio, si basa sull'ipotesi che l'umidità relativa del microambiente interno alla confezione (che si modifica per l'ingresso di vapore acqueo dall'esterno) sia immediatamente e sempre in equilibrio con quella del prodotto.

Scopo di tale lavoro è quello di verificare tale assunzione mediante l'utilizzo di sensori di umidità relativa che, posti all'interno di confezioni flessibili contenenti rondelle di mele disidratate e fette biscottate, sono in grado di monitorare in continuo ed in modo puntuale le variazioni di umidità all'interno del prodotto e nello spazio di testa delle confezioni.

Risultati preliminari ottenuti hanno negato l'ipotesi che l'umidità relativa del microambiente interno alla confezione sia immediatamente in equilibrio con quella del prodotto

Verification of shelf life predicting models for dried packaged products using relative moisture sensors

A shelf life model of packaged food product considers the variables product, packaging and environment. The reliability of the model is based on both the accuracy of the measures of the variables and the knowledge of their interactions. In many applications these models have shown to be reliable. However they are based on theoretical assumptions that have not yet been verified experimentally and that could induce errors. One of these assumptions, for example, assumes that the relative moisture of the packaging headspace (which changes with the entrance of water vapour from the outside) is immediately in equilibrium with the product.

Aim of this work is to verify this assumption by using relative moisture sensors placed inside packages of dehydrated apples and *fette biscottate*. The sensors are able to monitor continuously and in real time the moisture changes in the product and in the headspace of the packaging.

Preliminary results have denied the assumption that the relative moisture of the packaging headspace is immediately in equilibrium with the product.

Innovative approaches and instruments in modelling and monitoring the shelf life of packaged perishable foods

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Tutor: Prof. Luciano Piergiovanni

In this PhD thesis research chemical or physical indexes of food quality will be identified for defined products, in order to measure them with sensors. Sensors will be insert in food packages to collect data. On the basis of the collected data, existing shelf life prediction models will be incorporated and verified with mathematical software packages that can reproduce and predict the shelf life of products. New models will also be developed.

In a first phase relative moisture sensors will be used to verify and develop moisture depending models. In a second step RFID tags will be equipped with sensor. The use of RFID transmission technology will allow to take advantage of the non contact, non line of sight and real time communication mode.

Approcci e strumenti innovativi nella modellazione e nel controllo della shelf life di prodotti deperibili confezionati

In questo progetto di dottorato verranno identificati indicatori chimici o fisici di qualità di prodotti alimentari allo scopo di misurarli mediante sensori. I sensori verranno inseriti all'interno di confezioni alimentari e i dati raccolti verranno utilizzati per verificare e migliorare i modelli di previsioni della shelf life esistenti, mediante l'ausilio di software matematici capaci di riprodurre e predire tale shelf life. Saranno anche sviluppati nuovi modelli di previsione.

In una prima fase sensori di umidità relativa saranno usati per verificare e sviluppare modelli di previsione umidità dipendenti; successivamente tag RFID saranno equipaggiati con tali sensori. L'uso della tecnologia di trasmissione RFID consentirà una modalità di comunicazione in tempo reale, senza contatto e in assenza di campo visivo.

1. State-of-the-Art

Shelf life models are mathematical equations which describe the relationship between food, package, and environment. Shelf life models are useful to predict the shelf life of food, to design food packages, and to provide useful insights. The accuracy with which these relationships are measured influences the reliability of the models. It is also necessary to know the relationships among the variables that play a significant role in defining food quality.

Moisture depending models

Many chemical, biological, and physical changes are dependent on moisture content or water activity in the foods, whose changes may be dictated by the packaging protection from the environment in the distribution channel. Water activity is ruled by the moisture content in the food, which may change with time through the permeation process of water vapor across the packaging film. The equilibrium relationship between moisture content and water activity is explained by the sorption/desorption isotherm, which is obtained mostly by the experiments determining moisture contents of the food samples equilibrated under different relative humidity conditions. Many attempts were conducted to express the equilibrium relationship by mathematical forms. The most widely used are the equations of BET, GAB, Halsey, Henderson, Oswin, Khun, Inglesias, and Chirife (Lee *et al.*, 2008). These equations are used in forecast models to determinate the shelf life of moisture depending products. All these models assume that the relative moisture of the headspace of the packaging (which changes with the entrance of water vapour from the outside) is immediately in equilibrium with the product. They also assume that the transmission of vapour water through the packaging is directly proportional to the difference in relative humidity between the outside and the inside of the packaging and then gradually reduces, according to a linear relationship. Both these conditions have not yet been verified experimentally and are based on theoretical considerations (Piergiovanni, 2002).

Intelligent RFID

Intelligent RFID (Radio Frequency Identification) is the most promising concept to capture temperature and forward quality information without trapping into communication bottlenecks. This approach will probably not provide multi-factor quality parameters details like a main frame system but can still provide rapid information for immediate response at any step of the distribution chain. Although no hardware solution is currently available, the measurements of the required resources demonstrate that it would be possible to integrate the calculation of a shelf life model into an RFID logger (Jedermann *et al.*, 2007).

2. PhD Thesis Objectives and Milestones

- A1) **Identification and selection** of the product (A1.1) based on previous experimental experiences and considering the existing literature. Identification of the acceptability limits of the product (A1.2) and selection of the proper packaging solution for the chosen product (A1.3).
- A2) **Measurement system** assembly and calibration. The design and the implementation (A2.1) of the measuring system will be done with the collaboration of engineering companies. Sensors will be calibrated (A2.2) by appropriate procedures, defined by standard methods if available.
- A3) **Characterization of the product** by the determination of moisture content (A3.1), water activity (A3.2) and the construction of sorption/desorption isotherm (A3.3).
- A4) **Verification and validation** of the existing models and development of new models. On the basis of the collected data (A4.1), existing models will be verified (A4.2) and new models will be developed (A4.3).
- A5) **Reliability of the new model** will be checked comparing its prediction with the real shelf life of the product (A5.1) in order to determine its reliability and to implement appropriate corrections (A5.2).
- A6) **RFID tags** will be equipped with sensors (A6.1) and used in a real application to monitor shelf life (A6.2).
- A7) **Writing and Editing** of the PhD thesis, scientific papers, oral and/or poster communications.

Table 1 Gantt diagram for this PhD thesis project.

Activity	Months	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
A1) Identification and selection		■	■	■																					
1) Product		■	■	■																					
2) Limits																									
3) Package																									
A2) Measurement system			■	■	■	■	■	■																	
1) Design and implementation			■	■	■	■	■	■																	
2) Calibration																									
A3) Characterization of the product				■	■	■	■	■																	
1) Moisture content				■	■	■	■	■																	
2) Water activity				■	■	■	■	■																	
3) Sorption/desorption isotherm																									
A4) Verification and validation								■	■	■	■	■	■	■	■	■	■	■							
1) Data collection								■	■	■	■	■	■	■	■	■	■	■							
2) Model verification																									
3) Develop of new model																									
A5) Reliability of the new model															■	■	■	■	■	■	■	■	■	■	■
1) Comparing prediction															■	■	■	■	■	■	■	■	■	■	■
2) Corrections																									
A6) RFID tags																						■	■	■	■
1) Sensors application on RFID tags																						■	■	■	■
2) Real application																							■	■	■
A7) Thesis and Paper Preparation																									

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INNOVATIVE APPROACHES AND INSTRUMENTS IN MODELING AND MONITORING THE MOISTURE DIFFUSION IN PACKAGES AND MOISTURE ADSORPTION BY DRIED PRODUCTS

P. Lamiani, S. Limbo, L. Piergiovanni¹

ABSTRACT

Shelf life forecast models for moisture depending products assume that the relative humidity of the package headspace (which changes with the entrance of water vapour from the outside) is immediately in equilibrium with the product.

In the present research *fetta biscottata* (a typical Italian bakery product) has been used as a model system to evaluate how different quantities of product, different headspace volumes, and different packaging solutions influence the equilibrium between the relative humidity of the headspace and the relative humidity of the product.

From the data obtained it can be concluded that the relative humidity of the headspace of the packaging is not immediately in equilibrium with the product. The theoretical assumption generally used in the shelf life modeling has not been verified for this type of product.

KEY WORDS: humidity sensors, bakery products, shelf life modelling.

INTRODUCTION

Shelf life models are mathematical equations which describe the relationship between food, package, and environment. These models are based on different degradation factors and are useful to predict the shelf life of food, to design food packages, and to provide useful insights.

Many chemical, biological, and physical changes depend on moisture content or water activity in the foods, whose changes may be dictated by the packaging protection from the environment in the distribution channel. Water activity is ruled by the moisture content in the food, which may change with time through the permeation process of

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water vapor across the packaging film. The equilibrium relationship between moisture content and water activity is explained by the adsorption/desorption isotherm and several mathematical equations have been developed to express this equilibrium relationship (1). These equations are used in forecast models to determinate the shelf life of moisture depending products (2). All these models assume that the relative humidity of the package headspace (which change with the entrance of water vapour from the outside) is immediately in equilibrium with the product (3). This assumption has not yet been verified experimentally and cannot be valid for all the products and the packages.

The aim of the present work was to study if different quantities of product, different headspace volumes, and different packaging solutions may influence the equilibrium between the relative humidity of the headspace and of the product.

MATERIALS AND METHODS: An acquisition system composed by humidity sensors and a specific acquisition software to record simultaneously different moisture and temperatures values has been built in collaboration with RDE Company srl. Rigid trays (Sirap Gema) with capacity of 1400 and 1030 cm³ sealed with a OPP 20 mm film (Moplefan) have been used as a model package system. The water vapor transmission rate (WVTR) of the complete package has been determined, by means of a gravimetric method, as equal to $1.52 \pm 0.02 \text{ g pack}^{-1} 24\text{h}^{-1}$ (38°C and 98% ΔRH).

Fetta biscottata (a typical Italian bakery product, with a water activity of 0.22 and a moisture content of $3.71 \pm 0.27 \text{ g/100g}$) has been packed inside the trays in different quantities, at room air. The experiments were repeated at least two times for each sample.

Humidity sensors have been placed inside the product and in the headspace, in order to record the relative humidity in different points of the package.

The packages were submitted to an accelerated storage test in a thermostatic cell at $38 \pm 0.5^\circ\text{C}$ and 98% RH.

Different quantities of the dry product (*fetta biscottata*) have been packaged in the two type of trays, obtaining the combinations summarized in table 1.

RESULTS AND CONCLUSIONS

During the accelerated storage the moisture adsorption by *fetta biscottata* and the moisture increase in the headspace of the packages have been measured and recorded every 30 minutes for each combination. In figure 1 the relative humidity change for sample 1 is shown. The “Headspace” curve represents the moisture diffusion in the headspace, while the “Product” curve represents the moisture adsorption by *fetta biscottata*. For all the samples the difference between the curves can be considered constant in the RH range from 0 to 65% and shows the delay of the product in absorbing the moisture. Experiments conducted until 95% RH demonstrated that the two curves joint after a quite long time (data not shown).

To analyze the effect of the different packaging combinations, the ratio between the headspace volume and the product weight was related to the difference (in average) between the headspace and the product RH values. Data in table 1 show that the higher the ratios, the bigger the differences.

In figure 2 the differences in RH values are plotted versus the volume/weight ratio, showing a clear trend and an increasing uncertainty in the measures.

From our data, obtained combining different weights of *fetta biscottata* and different headspace volumes, it can be concluded that the relative humidity of the headspace of the packaging (which changes for the water vapour permeability) is not immediately in equilibrium with the product. The theoretical assumption generally used in the shelf life modeling has not been verified for this product and, in future works, it will be studied how these differences influence the shelf life prediction for *fetta biscottata* and for other moisture depending products and different packages.

ACKNOWLEDGMENTS

To RDE Company srl (Cormano, Milano, Italy) for the support and the hardware and software knowledge.

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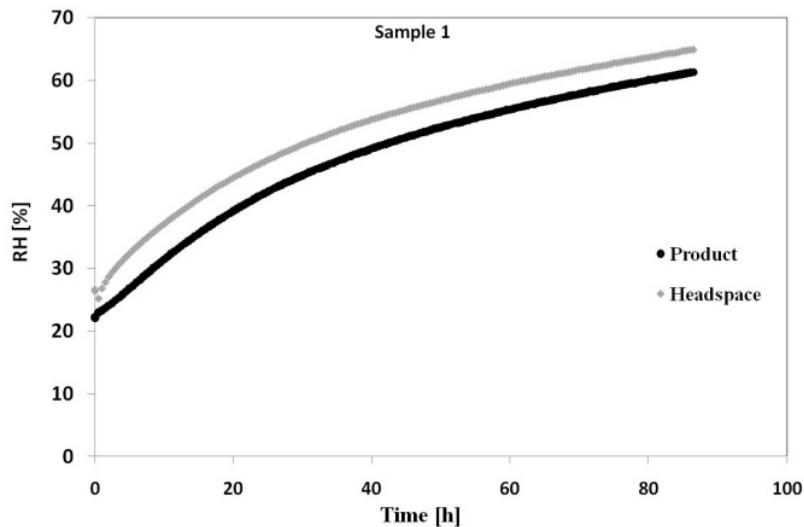


Figure 1: moisture change in sample 1

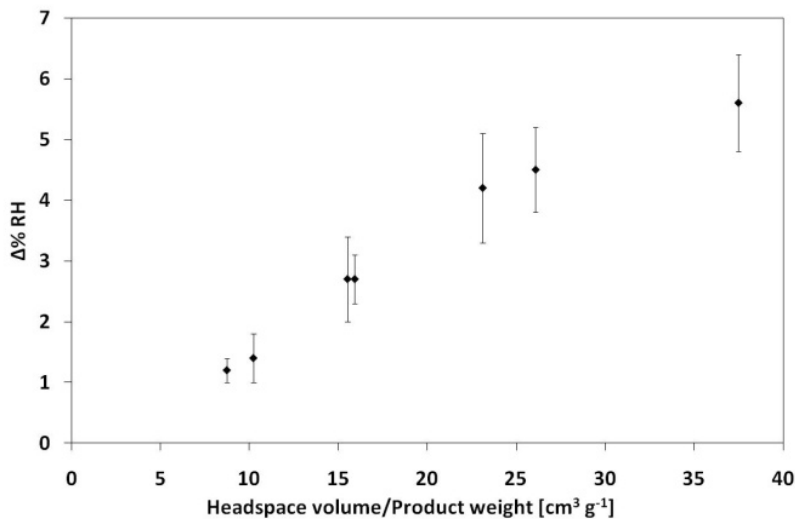


Figure 2: relationship between headspace volume and $\Delta\% \text{RH}$

Table 1: packaging combinations and RH differences among packaging solutions.

Sample number	Number of fetta biscottata	Product weight [g]	Product volume [cm ³]	Tray volume [cm ³]	Headspace volume [cm ³]	Headspace volume/Product weight [cm ³ g ⁻¹]	$\Delta\% \text{RH}$
1	4	32.48	182.8	1030	847.2	26.1	4.5±0.7
2	4	32.48	182.8	1400	1217.2	37.5	5.6±0.8
3	6	48.72	274.2	1030	755.8	15.5	2.7±0.7
4	6	48.72	274.2	1400	1125.8	23.1	4.2±0.9
5	8	64.96	365.6	1030	664.4	10.2	1.4±0.4
6	8	64.96	365.6	1400	1034.4	15.9	2.7±0.4
7	12	97.44	548.4	1400	851.6	8.7	1.2±0.2

Innovative approaches and instruments in modelling and monitoring the shelf life of packaged perishable foods

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The activities planned for the second year of the PhD thesis project are described. 1) The product was chosen, and its package was characterized. 2) The measurement and acquisition system has been designed, set up, and calibrated. 3) The chosen product (*Fetta biscottata*, a typical Italian bakery product) has been characterized in terms of water activity (a_w), moisture content, and sorption/desorption isotherm. 4) The measurement system has been used to record the moisture changes inside the package and the product. The data obtained have been used to verify the assumption on which the main moisture depending shelf life prediction models are based.

Approcci e strumenti innovativi nella modellazione e nel controllo della shelf life di prodotti deperibili confezionati

Le attività previste per il secondo anno di dottorato sono di seguito descritte. E' stato scelto il prodotto e sono state determinate le caratteristiche dell'imballaggio. Il sistema di misura è stato progettato, costruito e calibrato. Il prodotto selezionato (*Fetta biscottata*) è stato caratterizzato in termini di attività dell'acqua (a_w), contenuto umido e isoterma di assorbimento/desorbimento. In ultimo il sistema di misura è stato usato per rilevare la diffusione di umidità all'interno della confezione e del prodotto. I dati raccolti sono stati utilizzati per verificare l'assunzione teorica su cui sono basati i modelli di previsione della shelf life per prodotti umidità dipendenti.

Key words: humidity sensors, bakery products , shelf life modelling.

1. Introduction

According to the project previously described (Lamiani, 2009) the following activities were developed:

A1) Identification and selection of the product to be used for the experiments.

A2) Measurement system assembly and calibration.

A3) Characterization of the product by moisture content, a_w , and sorption/desorption isotherm construction.

A4) Verification and validation of the existing models and development of new models.

The fourth activity was previewed overlapped on the second and third year; only the first part with the data collection was done and reported in the present work.

2. Materials and Methods

The a_w of *fetta biscottata* was measured instrumentally at 38°C; the moisture content determined in a oven at 130°C for 1.5 h. Rigid EPS trays with capacity of 1400 and 1030 cm³ sealed with a OPP 20 µm film have been used as model package systems. The water vapor transmission rate (WVTR) of the package has been determined, by a gravimetric method, as equal to 1.52±0.02 g pack⁻¹ 24h⁻¹ (38°C and 98% ΔRH).

Fetta biscottata have been packed inside the trays in different quantities, using room air. Humidity sensors have been placed inside the product and in the headspace, in order to record the relative humidity in different points of the package and of the product. The packages were stored in a cell at 38±0.5°C and 98% RH.

3. Results and discussion

Fetta biscottata has been chosen for the regular shape and geometry, and for the uniformity among different packages. The acceptable maximum moisture content will be determined with a sensorial test in a following step. The acquisition system composed by humidity sensors and a specific acquisition software to record moisture values has been built in collaboration with RDE Company srl. It has been calibrated using saturated salt solutions at different relative humidity values: 0-11-23-32-44-52-79-92-97-100% (Bell and Labuza, 2000a).

The moisture content, water activity, and the sorption/desorption isotherm have been determined for *fetta biscottata*. The water activity was equal to 0.249±0.003 and the moisture content to 3.71±0.27 g/100g. The sorption/desorption isotherm was constructed at relative humidity values of 11-23-32-44-52-66-75-86-92% (Wolf *et al*, 1985). Different quantities of the dry product (*fetta biscottata*) have been packaged in the two type of trays, obtaining the combinations summarized in table 1.

During the accelerated storage the moisture adsorption by *fetta biscottata* and the moisture increase in the

headspace of the packages have been measured and recorded every 30 minutes for each combination. In figure 1 the moisture change for sample 1 is shown. The experiments were repeated at least two times for each sample.

The “Headspace” curve represents the moisture diffusion in the headspace, while the “Product” curve represents the moisture adsorption by *fetta biscottata*. For all the samples the difference between the curves can be considered constant in the RH range considered and shows the delay of the products in adsorbing the moisture. Experiments conducted until 95% RH demonstrated that the two curves joint after a quite long time.

To analyze the differences among the samples, the ratio between the headspace volume and the product weight was related to the difference (in average) between the headspace and the product RH values. The data in the last column of table 1 show that the higher the ratios, the bigger the differences.

In figure 2 the differences in RH values are plotted versus the volume/weight ratio, showing a clear trend and an increasing uncertainty in the measures. This trend is very likely correlated to the composition and to the texture of the product used and must be checked with other moisture sensitive products.

From our data, obtained combining different weights of *fetta biscottata* and different headspace volumes, it can be concluded that the relative humidity of the headspace of the packaging (which changes for the water vapour permeability) is not immediately in equilibrium with the product. The theoretical assumption generally used in the shelf life modeling (Fava *et al.*, 2000) has not been verified for this product and in the third year it will be studied how these differences influence the shelf life prediction for *fetta biscottata* and for other moisture depending products and different packages.

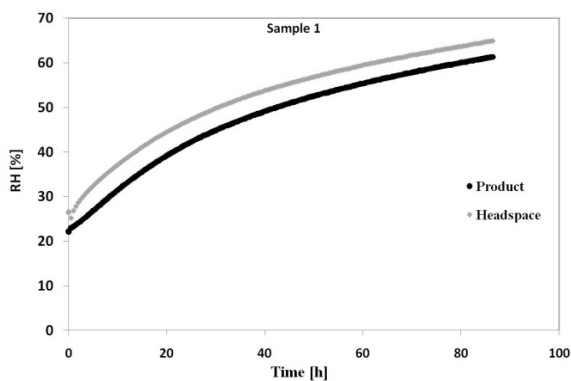


Figure 1: moisture change in sample 1

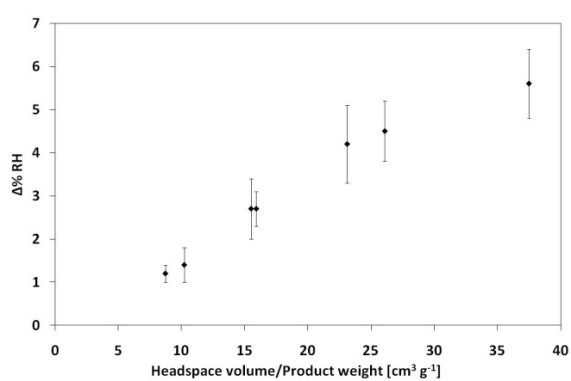


Figure 2: relationship between headspace volume and Δ% RH

Table 1: packaging combinations and RH differences among packaging solutions.

Sample number	Number of <i>fetta biscottata</i>	Product weight [g]	Product volume [cm ³]	Tray volume [cm ³]	Headspace volume [cm ³]	Headspace volume/Product weight [cm ³ g ⁻¹]	Δ% RH
1	4	32.48	182.8	1030	847.2	26.1	4.5±0.7
2	4	32.48	182.8	1400	1217.2	37.5	5.6±0.8
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7	12	97.44	548.4	1400	851.6	8.7	1.2±0.2

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Approcci e strumenti innovativi nella modellazione e nel controllo della shelf life di prodotti deperibili confezionati

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INTRODUZIONE

I modelli di previsione della shelf life sono equazioni matematiche che descrivono le relazioni che intercorrono tra il prodotto alimentare, la confezione e l'ambiente esterno. Tali modelli si basano su differenti fattori di degradazione e sono utili per predire la shelf life di un prodotto alimentare, per progettare gli imballaggi ma anche per fornire utili indicazioni sulle interazioni prodotto-imballaggio. Numerosi fenomeni chimici, biologici e fisici dipendono dal contenuto umido e dall'attività dell'acqua (a_w) dei prodotti alimentari. Tali fenomeni, durante la distribuzione commerciale, possono essere controllati dalla protezione offerta dall'imballaggio. L'attività dell'acqua è regolata dal contenuto umido del prodotto, che può aumentare nel tempo per via della permeabilità al vapor acqueo della confezione. La relazione di equilibrio tra il contenuto umido e l'attività dell'acqua (umidità relativa all'equilibrio) è espressa dall'isoterma di adsorbimento/desorbimento e diverse equazioni matematiche sono state elaborate per descriverla opportunamente (1). Tali equazioni sono utilizzate nei modelli di previsione della shelf life per prodotti umidità-dipendenti (2). Tutti i suddetti modelli si basano sull'assunzione teorica che l'umidità relativa (UR) dello spazio di testa della confezione, che aumenta per l'ingresso di vapor d'acqua dall'ambiente circostante, sia immediatamente in equilibrio con l'umidità relativa del prodotto (3). Questa assunzione non è mai stata verificata sperimentalmente e potrebbe non essere valida per tutti i prodotti e tutte le soluzioni di confezionamento.

SCOPO

Scopo del presente lavoro è quello di studiare come differenti quantità di prodotto, differenti spazi di testa e differenti soluzioni di confezionamento possano influenzare l'equilibrio tra l'umidità relativa del prodotto e quella dello spazio di testa.

MATERIALI E METODI

Fette biscottate: sono state utilizzate fette biscottate dorate acquistate presso la GDO. Le fette biscottate sono state caratterizzate determinandone l'umidità relativa ($UR=0.249\pm 0.003$), il contenuto umido ($M=3.71\pm 0.27g/100g$) e

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l'isoterma di adsorbimento /desorbimento, costruita condizionando il prodotto ai seguenti valori di umidità relativa mediante soluzioni saline sature: 11-23-32-44-52-66-75-86-92% (4).

Sistema di acquisizione: (Figura 1) il sistema di acquisizione dell'umidità relativa è stato ideato e costruito in collaborazione con RDE Company srl ed è composto da sensori di umidità collegati ad uno specifico software in grado di registrare i segnali acquisiti. Il sistema è stato calibrato a diversi valori di umidità relativa: 0-11-23-32-44-52-79-92-97-100% (5).

Film plastico: film trasparente di OPP 20 (polipropilene orientato, spessore 20 µm) prodotto dalla Moplefan.

Vaschette: vaschette in polistirene espanso di capacità 1400 e 1030 cm³ rivestite con un film a barriera totale, prodotte da Sirap Gema.

Prove di conservazione simulata: Le prove di conservazione simulata sono state effettuate in celle termostate FOC 225 a 38±0.5°C. Sul fondo delle vaschette di polipropilene è stata posizionata acqua demineralizzata, in quantità di circa 1 L, in modo da ottenere una umidità relativa interna del 98%.

RISULTATI E DISCUSSIONE

Le fette biscottate sono state scelte per la forma e la geometria regolare e costante tra i vari lotti.

Differenti quantità di prodotto sono state confezionate nelle due diverse tipologie di vaschette, ottenendo le combinazioni riportate in tabella 1.

Durante la conservazione in condizioni accelerate, per ciascuna combinazione, è stato misurato e registrato ogni 30 minuti l'assorbimento di umidità da parte delle fette biscottate e l'incremento di umidità nello spazio di testa. In figura 2 è visibile l'andamento dell'umidità nel tempo per il campione 1. Le prove sono state ripetute almeno due volte per ciascun campione.

La curva "Spazio di testa" rappresenta la diffusione dell'umidità nello spazio di testa, mentre la curva "Prodotto" rappresenta l'assorbimento da parte delle fette biscottate. Per tutti i campioni la differenza tra le due curve può essere ritenuta costante nell'intervallo di umidità considerato e mostra il ritardo con cui il prodotto assorbe l'umidità rispetto allo spazio di testa. Prove condotte fino a valori di UR pari al 95% dimostrano che le due curve tendono a coincidere solo dopo un considerevole lasso di tempo.

Per analizzare le differenze tra i campioni è stato calcolato il rapporto tra il volume dello spazio di testa ed il peso del campione. Tale rapporto è poi stato messo in relazione alla differenza (in media) tra i valori di umidità relativa dello spazio di testa e del prodotto. La tabella 1 mostra come all'aumentare del rapporto aumenta anche la differenza di umidità relativa.

Questo fenomeno è spiegato dalla resistenza dello "stagnant air layer" (6) all'interno della confezione, che ostacola la diffusione dell'umidità.

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In figura 3 sono rappresentate le differenze di umidità relativa correlate al rapporto volume/peso. Il grafico mostra un andamento crescente ed un incremento dell'incertezza nelle misure. Ciò è verosimilmente correlato alla composizione ed alla struttura del prodotto utilizzato e dovrà essere verificato utilizzando altri prodotti sensibili all'umidità.

Dai dati ottenuti combinando differenti quantità di fette biscottate e differenti volumi di spazio di testa, è possibile concludere che l'umidità relativa dello spazio di testa (che aumenta per via della permeabilità della confezione) non è immediatamente in equilibrio con quella del prodotto. L'assunzione teorica utilizzata nei modelli di previsione della shelf life umidità-dipendenti non è verificata per questo tipo di prodotti. In lavori successivi verrà studiato come queste differenze influiscano sulla previsione di shelf life per le fette biscottate e per altri prodotti sensibili agli scambi di umidità.

RINGRAZIAMENTI

A RDE Company srl (Cormano, Milano, Italy) per il supporto e per lo sviluppo dell'hardware e del software.

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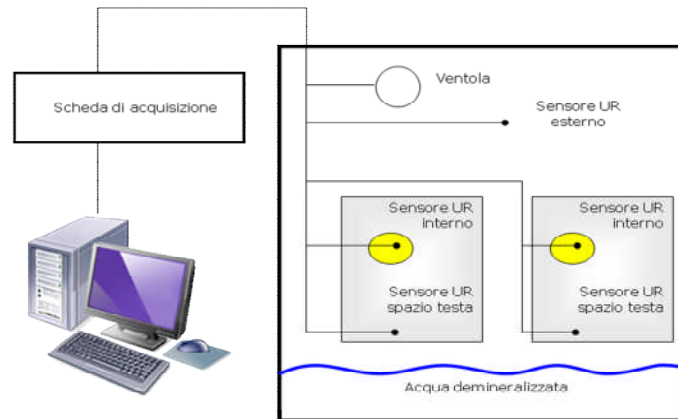


Figura 1: schema del sistema di acquisizione

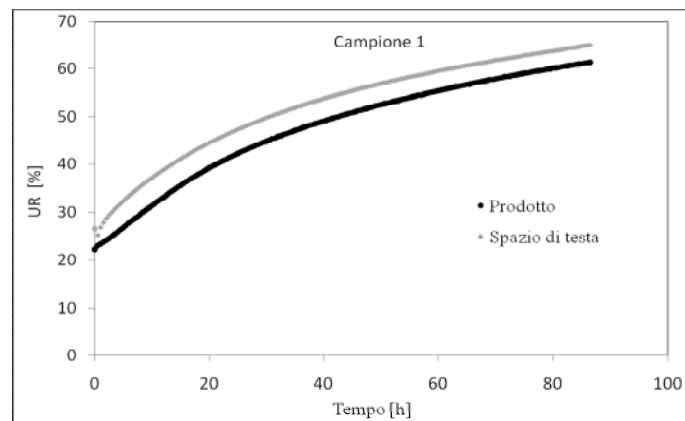


Figura 2: assorbimento umidità nel campione 1

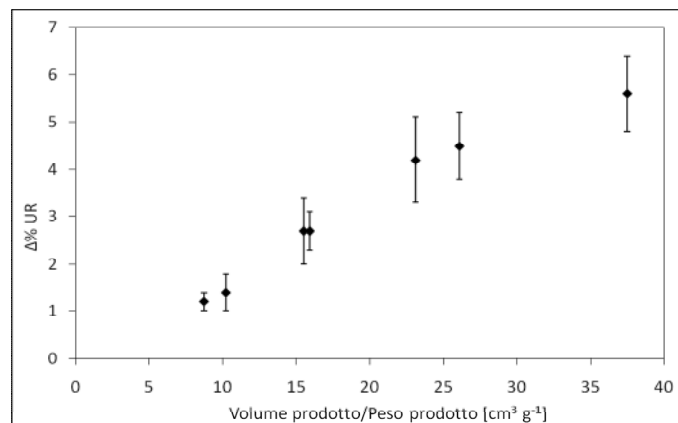


Figura 3: correlazione tra lo spazio di testa e $\Delta UR\%$

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Numero campione	Numero di fette biscottate	Peso prodotto [g]	Volume prodotto [cm ³]	Volume vaschetta [cm ³]	Volume spazio di testa [cm ³]	Volume prodotto /Peso prodotto [cm ³ g ⁻¹]	Δ% RU
1	4	32.48	182.8	1030	847.2	26.1	4.5±0.7
2	4	32.48	182.8	1400	1217.2	37.5	5.6±0.8
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7	12	97.44	548.4	1400	851.6	8.7	1.2±0.2

Tabella 1: combinazioni di confezionamento

Approcci e strumenti innovativi nella modellazione e nel controllo della shelf life di prodotti deperibili confezionati.

I modelli di previsione della shelf life sono equazioni matematiche che descrivono le relazioni che intercorrono tra il prodotto alimentare, l'imballaggio e l'ambiente. Numerosi fenomeni chimici, biologici e fisici dipendono dall'umidità relativa dei prodotti alimentari. L'umidità relativa è a sua volta strettamente correlata al contenuto umido del prodotto e può variare nel tempo per via della permeabilità della confezione.

I modelli di previsione umidità-dipendenti si basano sull'assunzione teorica che l'umidità relativa dello spazio di testa sia immediatamente in equilibrio con quella del prodotto.

Scopo del presente lavoro è verificare le assunzioni teoriche alla base dei modelli di previsione della shelf life umidità-dipendenti, studiando come differenti quantità di prodotto, differenti spazi di testa e differenti soluzioni di imballaggio possano influire sull'equilibrio tra l'umidità relativa dello spazio di testa e quella del prodotto.

I risultati ottenuti mostrano come, nel caso del sistema modello, l'umidità relativa dello spazio di testa non sia immediatamente in equilibrio con quella del prodotto, negando quindi l'assunzione teorica.

Innovative approaches and instruments in modelling and monitoring the shelf life of packaged perishable foods

Shelf life forecast models for moisture depending products assume that the relative humidity of the package headspace (which changes with the entrance of water vapour from the outside) is immediately in equilibrium with the product.

In the present research *fetta biscottata* (a typical Italian bakery product) has been used as a model system to evaluate how different quantities of product, different headspace volumes, and different packaging solutions influence the

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equilibrium between the relative humidity of the headspace and the relative humidity of the product.

From the data obtained it can be concluded that the relative humidity of the headspace of the packaging is not immediately in equilibrium with the product. The theoretical assumption generally used in the shelf life modeling has not been verified for this type of product.

Applicazione di un modello di previsione della shelf life umidità-dipendente su un prodotto da forno

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INTRODUZIONE

I modelli di previsione della shelf life sono equazioni matematiche che descrivono le relazioni che intercorrono tra il prodotto alimentare, la confezione e l'ambiente esterno. Tali modelli si basano su differenti fattori di degradazione e sono utili per predire la shelf life di un prodotto alimentare, per progettare gli imballaggi ma anche per fornire utili indicazioni sulle interazioni prodotto-imballaggio. Numerosi fenomeni chimici, biologici e fisici dipendono dal contenuto umido e dall'attività dell'acqua (a_w) dei prodotti alimentari. Tali fenomeni, durante la distribuzione commerciale, possono essere controllati dalla protezione offerta dall'imballaggio. L'attività dell'acqua è regolata dal contenuto umido del prodotto, che può aumentare nel tempo per via della permeabilità al vapor acqueo della confezione. La relazione di equilibrio tra il contenuto umido e l'attività dell'acqua è espressa dall'isoterma di adsorbimento/desorbimento e diverse equazioni matematiche sono state elaborate per descriverla opportunamente (1). Tali equazioni sono utilizzate nei modelli di previsione della shelf life per prodotti umidità-dipendenti (2).

SCOPO

Scopo del presente lavoro è applicare un modello di previsione della shelf life umidità-dipendente ad una specifica categoria di prodotti da forno caratterizzati dallo stesso processo tecnologico ma da diversa formulazione e verificare come la composizione influisca sulla shelf life del prodotto stesso a parità di confezione.

MATERIALI E METODI

Fette biscottate: sono state utilizzate tre diverse tipologie di fette biscottate (Dorate, Cereali, Integrali), tutte prodotte da Mulino Bianco (Barilla), acquistate presso la GDO. Le tre tipologie di fette sono state caratterizzate determinandone l'attività dell'acqua, il contenuto umido e le dimensioni, dati riportati in Tabella 1. Per ciascuna tipologia è stata costruita l'isoterma di adsorbimento/desorbimento (3), condizionando il prodotto a differenti valori di

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umidità relativa mediante soluzioni saline sature ed ottenendo i rispettivi valori di contenuto umido M (g H₂O/g SS) come riportato in Tabella 2 (4).

Confezione fette biscottate: le fette biscottate sono venute all'interno di due parallelepipedi di cartoncino ondulato ricoperti da uno strato di carta. I due parallelepipedi a loro volta sono contenuti in un film di PP saldato che li avvolge. La permeabilità, o WVTR (Water Vapour Transmission Rate), dell'intero imballaggio è stata determinata mediante metodo gravimetrico ed è risultata essere pari a $0.2 \pm 0.02 \text{ g pack}^{-1} 24\text{h}^{-1}$ (25°C e 90% UR).

Software interpolazione: i punti sperimentali ottenuti sono stati interpolati con il software TableCurve 2D v4 della Jandel Scientific Software.

Attività dell'acqua: l'attività dell'acqua delle fette biscottate è stata misurata mediante lo strumento Novasina LabMaster aw (Novasina AG, Svizzera) termostato a $25 \pm 0,2^\circ\text{C}$, posizionando il prodotto nell'apposito alloggiamento e leggendo il valore all'equilibrio (Tabella 1).

Contenuto umido: il contenuto umido delle fette biscottate è stato determinato misurando la perdita di peso dei campioni dopo 90 minuti di permanenza in stufa a 130°C (Tabella 1).

Modello previsione della shelf life: il modello di previsione della shelf life è stato implementato mediante un foglio di calcolo di Microsoft Excel.

RISULTATI E DISCUSSIONE

I punti sperimentali ottenuti condizionando le fette biscottate (Tabella 2 e Figura 1) sono stati interpolati con le equazioni di Oswin, Smith, Iglesias-Chirife, Henderson e Halsey (1) utilizzando il software Table Curve. La miglior equazione interpolante per tutte e tre le tipologie di fette biscottate è risultata essere l'equazione di Oswin, mostrando per le fette Dorate un $R^2=0.994$ ed un errore percentuale medio $E\%=4.825$, per le Cereali un $R^2=0.989$ ed un $E\%=5.972$ e per le Integrali un $R^2=0.997$ ed un $E\%=4.618$ (Tabella 3).

L'equazione di Oswin è stata quindi selezionata per descrivere la relazione che lega il contenuto umido e l'attività dell'acqua per le tre tipologie di fette biscottate ed è stata quindi implementata nel modello di previsione della shelf life. Nel modello di previsione sono stati inoltre inseriti tutti i parametri relativi al prodotto (peso, contenuto umido, attività dell'acqua), alla confezione (WVTR) e all'ambiente (Temperatura di 25°C e UR del 90%).

Ipotizzando un'umidità relativa limite per le fette biscottate pari al 40%, la shelf life stimata per le fette biscottate Dorate è risultata essere di 71 giorni, per le Cereali di 56 giorni e per le Integrali di 27 giorni.

Per ottenere questo risultato si sono dovute costruire tre isoterme e valutare la capacità interpolante di cinque equazioni. Per provare ad ottimizzare il

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procedimento si è quindi provato a costruire una sola isoterma di adsorbimento/desorbimento per le tre tipologie di fette biscottate interpolando tutti insieme i punti sperimentali ottenuti mediante le stesse cinque equazioni. La miglior equazione interpolante è risultata essere, anche in questo caso, quella di Oswin mostrando un $R^2=0.935$ ed un $E\%=19.589$ (Tabella 3), valori che indicano una scarsa capacità interpolante, che infatti è stata evidenziata dalla relativa previsione della shelf life mostrando un errore pari al 18% per le fette Dorate rispetto all'uso di una isoterma singola dedicata, del 44% per le Cereali e del 148% per le Integrali, sconsigliandone quindi l'applicazione.

Si è quindi provato ad interpolare, mediante l'equazione di Oswin, i punti sperimentali abbinando le tipologie di fette biscottate a due a due: Dorate-Cereali, Cereali-Integrali, Dorate-Integrali. In Tabella 4 sono visibili gli indici statistici ottenuti, evidenziando come per le fette Dorate e Cereali sia possibile usare una isoterma unica avendo l'eq. equazione interpolante un $R^2=0.990$ ed un $E\%=5.819$ mentre ciò non è possibile per le altre due coppie, poiché gli indici statistici evidenziano una scarsa capacità interpolante.

La previsione di shelf life per le fette Dorate e Cereali, utilizzando un'isoterma di adsorbimento unica e comune alle due tipologie, è risultata essere rispettivamente di 76 e 51 giorni, mostrando un errore rispetto alla previsione ottenuta con l'isoterma singola dedicata del 7 e 9%, valori ritenuti accettabili.

Tale lavoro ha evidenziato come negli studi di modellazione della shelf life sia necessario caratterizzare al meglio i prodotti oggetti di studio ed i relativi imballaggi, la necessità di costruire in maniera accurata l'isoterma di adsorbimento dei prodotti e l'importanza degli indici statistici e della loro corretta interpretazione. Un tal approccio può consentire di valutare la possibilità di semplificare il lavoro utilizzando isoterme comuni per tipologie di prodotto simili tra loro e appartenenti alla stessa categoria ma caratterizzati da diversa formulazione.

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	Dorate	Cereali	Integrali
Peso totale [g]	365	345	336
Peso singola fetta [g]	8.12±0.17	10.24±0.39	7.67±0.34
Quantità	40	32	40
Altezza singola fetta [mm]	70.7±0.1	70.9±0.1	70.7±0.1
Larghezza singola fetta [mm]	67.7±0.6	69.8±0.3	68.0±0.1
Spessore singola fetta [mm]	0.9±0.1	11.3±0.3	0.9±0.1
Attività dell'acqua	0.250±0.003	0.307±0.003	0.198 ±0.003
Contenuto umido [g/100g]	3.712±0.271	4.864±0.037	3.2828±0.066

Tabella 1: caratterizzazione fette biscottate.

aw	M (g H ₂ O/g SS) Dorate	M (g H ₂ O/g SS) Cereali	M (g H ₂ O/g SS) Integrali
0,114	0.0381	0.0441	0.0154
0,241	0.0510	0.0583	0.0317
0,331	0.0603	0.0639	0.0356
0,438	0.0751	0.0773	0.0464
0,529	0.0879	0.0964	0.0662
0,691	0.1281	0.1265	0.0955
0,753	0.1499	0.1477	0.1208
0,841	0.2076	0.2039	0.1773

Tabella 2: valori sperimentali per costruzione isoterma di adsorbimento/desorbimento.

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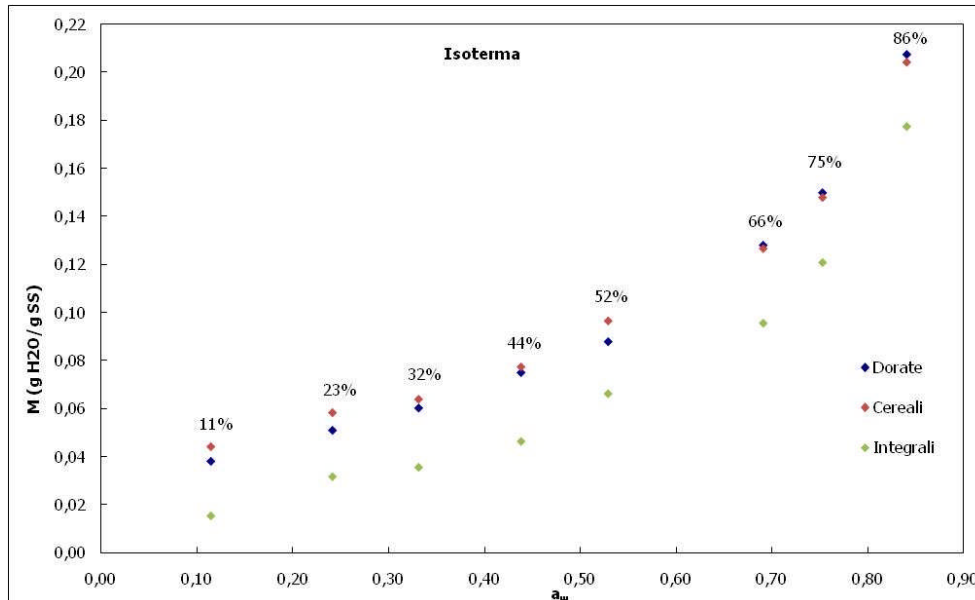


Figura 1: punti sperimentali isoterma di adsorbimento/desorbimento.

	Dorate	Cereali	Integrali	Dorate Cereali Integrali
Oswin	R ² =0.994 E%=4.825	R ² =0.989 E%=5.972	R ² =0.997 E%=4.618	R ² =0.935 E%=19.589
Smith	R ² =0.989 E%=5.248	R ² =0.987 E%=6.867	R ² =0.982 E%=11.085	R ² =0.927 E%=21.606
Igl-Chirife	R ² =0.981 E%=8.842	R ² =0.981 E%=7.668	R ² =0.985 E%=13.160	R ² =0.924 E%=23.416
Henderson	R ² =0.971 E%=11.157	R ² =0.960 E%=10.873	R ² =0.984 E%=12.931	R ² =0.914 E%=21.058
Halsey	R ² =0.838 E%=27.815	R ² =0.738 E%=31.089	R ² =0.971 E%=12.276	R ² =0.821 E%=25.278

Tabella 3: indici statistici interpolazione punti sperimentali.

	Dorate Cereali	Cereali Integrali	Dorate Integrali
Oswin	R ² =0.990 E%=5.819	R ² =0.921 E%=23.807	R ² =0.937 E%=18.919

Tabella 4: indici statistici interpolazione punti sperimentali.

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**Applicazione di un modello di previsione della shelf life umidità-
dipendente su un prodotto da forno**

I modelli di previsione della shelf life sono equazioni matematiche che descrivono le relazioni che intercorrono tra il prodotto alimentare, l'imballaggio e l'ambiente. Tali modelli si basano su diversi fattori di degradazione e sono utili per predire la shelf life degli alimenti e per ottimizzare la progettazione degli imballaggi.

Scopo del presente lavoro è applicare un modello di previsione della shelf life umidità-dipendente ad una specifica categoria di prodotti da forno caratterizzati dallo stesso processo tecnologico ma da diversa formulazione e verificare come la composizione influisca sulla shelf life del prodotto stesso a parità di confezione.

I dati ottenuti hanno mostrato la necessità di caratterizzare al meglio i prodotti oggetti di studio ed i relativi imballaggi, dell'accuratezza nella costruzione dell'isoterma di adsorbimento e l'importanza degli indici statistici e della loro corretta interpretazione per la valutazione e la semplificazione del lavoro di previsione della shelf life.

Application of a shelf life moisture depending model to a bakery product

Shelf life models are mathematical equations which describe the relationship between food, package, and environment. These models are based on different degradation factors and are useful to predict the shelf life of food, to design food packages, and to provide useful insights.

Aim of the present work is to apply a shelf life moisture depending model to a specific category of bakery product to analyze how different formulation may influence the shelf like prediction. The chosen products are characterized by the same technological process and package, but have a different ingredient formulation.

The data obtained showed the importance of the correct characterization of the products and its packaging, the importance of the accuracy in the construction of the adsorption isotherm and the importance of statistical indexes and their correct use for the shelf life prediction.

Innovative approaches and instruments in modelling and monitoring the shelf life of packaged perishable foods

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The aim of this PhD thesis is to verify the theoretical assumption assumed by moisture depending prediction models. This assumption states that the relative moisture of the headspace of the packaging (which changes with the entrance of water vapour from the outside) is immediately in equilibrium with the product.

In the present work a model system is used to study how different quantities of product, different headspace volumes, and different packaging solutions influence the equilibrium between the relative humidity of the headspace and of the product and how this difference influences the shelf life prediction.

Approcci e strumenti innovativi nella modellazione e nel controllo della shelf life di prodotti deperibili confezionati

Scopo di questa tesi di dottorato è la verifica dell'assunzione teorica alla base dei modelli di previsione della shelf life per prodotti umidità dipendenti. Tale assunzione afferma che l'umidità relativa dello spazio di testa della confezione (che aumenta con l'ingresso dell'umidità dall'esterno) è immediatamente in equilibrio con l'umidità relativa del prodotto.

Nel presente lavoro un sistema modello è stato utilizzato per studiare come differenti quantità di prodotto, differenti spazi di testa e differenti soluzioni di confezionamento possano influenzare l'equilibrio tra l'umidità relativa del prodotto e quella dello spazio di testa e come queste differenze incidano sulla previsione della shelf life.

Key words: humidity sensors, bakery products, shelf life modelling.

1. Introduction

According to the PhD thesis project previously described (Lamiani, 2009) this communication reports the main results of the following activities that were developed:

A3) Characterization of the packaging system and product characteristics determination: dimensions, moisture content, water activity and sorption/desorption isotherm construction.

A4) Data collection, application of a shelf life moisture depending prediction model and, on the basis of the obtained data, correction of the shelf life prediction model.

2. State of the Art

Shelf life models are mathematical equations which describe the relationship between food, package, and environment. Shelf life models are useful to predict the shelf life of food, to design food packages, and to provide useful insights. The accuracy by which these relationships are measured influences the reliability of the models. It is also necessary to know the relationships among the variables that play a significant role in defining food quality.

Moisture depending models

Many chemical, biological, and physical changes are dependent on moisture content or water activity in foods, whose changes may be dictated by the packaging protection from the environment in the distribution channel. Water activity is ruled by the moisture content in the food, which may change with time through the permeation process of water vapor across the packaging film. The equilibrium relationship between moisture content and water activity is explained by the sorption/desorption isotherm, which is obtained mostly by the experiments determining moisture contents of the food samples equilibrated under different relative humidity conditions. Many attempts were conducted to express the equilibrium relationship by mathematical forms. The most widely used are the equations of Smith, Halsey, Henderson, Oswin, Inglesias, and Chirife (Lee *et al.*, 2008). These equations are used in forecast models to determine the shelf life of moisture depending products. All these models assume that the relative moisture of the headspace of the packaging (which changes with the entrance of water vapour from the outside) is immediately in equilibrium with the product. This condition has not yet been verified experimentally and is based on theoretical considerations (Fava *et al.*, 2000).

2. Materials and Methods

Fetta biscottata, a typical Italian bakery product, has been chosen because its regular shape and geometry, and the uniformity among different packages. The acceptable maximum moisture content has been set at a relative humidity (RH) of 40%.

The water activity (a_w) of *fetta biscottata* was measured at 25°C with a Novasina LabMaster aw (Novasina AG, Switzerland); the moisture content (M) determined in an oven at 130°C for 1.5 h.

Rigid EPS trays of 1400 and 1030 cm³ capacity, sealed with a OPP 20 µm film, have been used as model package systems. The water vapor transmission rate (WVTR) of the package has been determined, by a gravimetric method (25°C and 98% ΔRH), as equal to 0.54±0.03 g pack⁻¹ 24h⁻¹ for the 1400 cm³ tray and to 0.41±0.02 g pack⁻¹ 24h⁻¹ for the 1030 cm³ tray.

An acquisition system composed by humidity sensors and a specific acquisition software to record moisture values has been assessed in collaboration with RDE Company srl (Lamiani, 2010).

Fetta biscottata have been packed inside the trays in different quantities, using room air. Humidity sensors have been placed inside the product and in the headspace, in order to record the relative humidity in different points of the package and of the product. The packages were stored in a thermostatic cell at 25±0.5°C and 98±0.5% RH.

3. Results and discussion

The moisture content and the water activity have been determined for *fetta biscottata*. The water activity was equal to 0.251±0.003 and the moisture content to 3.71±0.27 g/100g.

Different quantities of the dry product (*fetta biscottata*) have been packaged in the two type of trays, obtaining the combinations summarized in table 1. During the accelerated storage the moisture adsorption by *fetta biscottata* and the moisture increase in the headspace of the packages have been measured and recorded every 30 minutes for each combination. In figure 1 and 2 the moisture changes for sample 2 and 6 is shown. The experiments were repeated at least two times for each sample.

The “Headspace” curve represents the moisture diffusion in the headspace, while the “Product” curve represents the moisture adsorption by *fetta biscottata*. For all the samples the difference between the curves can be considered constant in the considered RH range and it shows the delay of the products in adsorbing the moisture. Experiments conducted until 95% RH demonstrated that the two curves joint after a quite long time.

To analyze the differences among the samples, the ratio between the headspace volume and the product weight was related to the difference (in average) between the headspace and the product RH values. Previous experiments conducted at 38°C demonstrated that the higher the ratios, the bigger the differences (Lamiani, 2010). The data showed an increasing trend and an increasing uncertainty in the measures, not allowing to determine exactly the relationships between the variables considered.

New experiments conducted at 25°C gave the results reported in table 1. In figure 3 the differences in RH values are plotted versus the volume/weight ratio, showing a linear relationship (in the range considered) between the ratio headspace volume/product weight and the headspace and product Δ% RH:

$$\Delta RH = 0.118 \times \frac{V_{\text{Headspace}}}{W_{\text{product}}} + 1.1669 \quad (1)$$

From our data, obtained combining different weights of *fetta biscottata* and different headspace volumes, it can be concluded that the relative humidity of the headspace of the packaging (which changes for the water vapour permeability) is not immediately in equilibrium with the product. The theoretical assumption generally used in the shelf life modeling (Fava *et al*, 2000) has not been verified for this product.

Table 1: packaging combinations and RH differences among packaging solutions.

Sample number	Number of <i>fetta biscottata</i>	Product weight [g]	Product volume [cm ³]	Tray volume [cm ³]	Headspace volume [cm ³]	Headspace volume/Product weight [cm ³ g ⁻¹]	Δ% RH
1	4	32.48	182.8	1030	847.2	26.1	4.5±0.6
2	4	32.48	182.8	1400	1217.2	37.5	5.6±1.5
3	6	48.72	274.2	1030	755.8	15.5	2.9±0.5
4	6	48.72	274.2	1400	1125.8	23.1	3.6±0.6
5	8	64.96	365.6	1030	664.4	10.2	2.5±0.3
6	12	97.44	548.4	1400	851.6	8.7	2.2±0.3

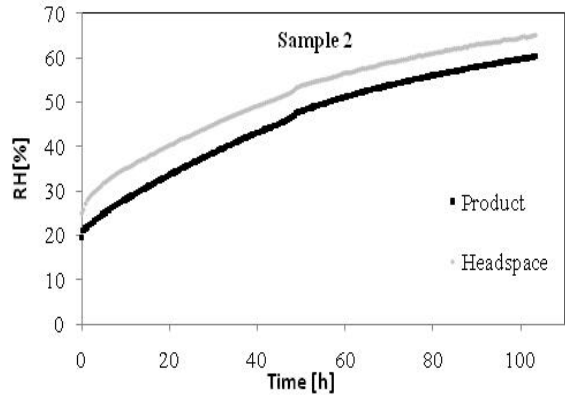


Figure 1: moisture change in sample 2.

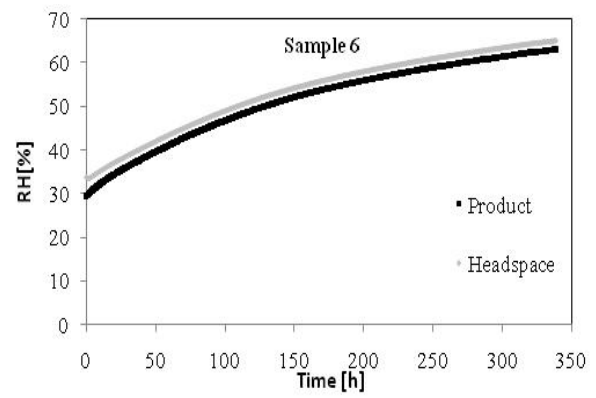


Figure 2: moisture change in sample 6

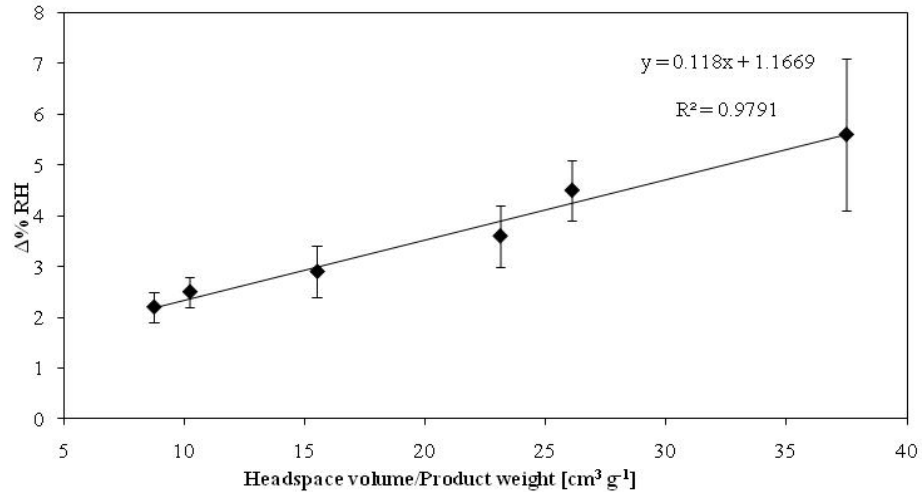


Figure 3: relationship between headspace volume and $\Delta\% \text{ RH}$

The water vapour sorption/desorption isotherm for *fetta biscottata* was determined according to the static, gravimetric method developed by COST-90 Project (Wolf *et al.*, 1985) and described by Bell and Labuza (2000). Based on the equilibrium moisture content at a given water activity, the sorption/desorption curve at 25°C for *fetta biscottata* was obtained fitting experimental data by the equations (Lee *et al.*, 2008) of Oswin (2), Smith (3), Iglesias-Chirife (4), Henderson (5) and Halsey (6) using the Table Curve 2D software:

$$M = a \times [a_w \times (1 - a_w)]^{1/b} \quad (2)$$

$$M = a - [b \times \ln(1 - a_w)] \quad (3)$$

$$M = a \times \left(\frac{a_w}{1 - a_w} \right) + b \quad (4)$$

$$M = \left[\frac{-\ln(1 - a_w)}{a} \right]^{1/b} \quad (5)$$

$$M = \left(-\frac{a}{\ln a_w} \right)^{1/b} \quad (6)$$

In order to identify the equation that better fitted the experimental data, the correlation coefficient (r^2) and the mean relative percentage deviation modulus ($\bar{E}\%$), calculated with the formula (7), were considered.

$$\bar{E}\% = \frac{100}{N} \sum_{i=1}^N \left| \frac{M_e - M_p}{M_e} \right| \quad (7)$$

where:

N = number of experimental data

M_e = moisture content experimental value

M_p = moisture content predicted value

The statistical parameters obtained for the different equations are listed in table 2:

Table 2: statistical parameters for the fitted equations.

Equation	r^2	$\bar{E}\%$
Oswin	0.99	4.83
Smith	0.99	5.25
Iglesias-Chirife	0.98	8.84
Helderson	0.97	11.16
Halsey	0.84	27.82

A $\bar{E}\%$ value below 10% indicates a reasonably good fit and values below 5% represent an extremely good fitting for practical purposes (Lomauro *et al.*, 1985). According to r^2 and $\bar{E}\%$ values, the best fittings was obtained for the Oswin equation, as evidenced in table 2. The statistical parameters calculated for the other equations showed that these equations did not provide a good fitting of the experimental data. Oswin equation was selected to interpolate the experimental points of the sorption/desorption isotherm.

To evaluate how the difference between the headspace and the product RH values influences the shelf life prediction, a shelf life prediction model has been applied to the product and package considered. For these type of moisture sensitive products the prediction models are based on the the water amount that permeates through the packaging film in a time unit. This value is a function of the package characteristics (permeability coefficient of the material KP , thickness l , and area exposed to the mass flux A) and of the driving force (Δp), according to the expression:

$$\frac{dQ}{dt} = \frac{KP_{H_2O}}{l} \cdot A \cdot \Delta p \quad (8)$$

In order to solve the differential equation (8), the model was implemented in a spreadsheet (Microsoft Office Excel 2007), in which all the variables related to the product (M , a_w , weight), the package (Kp , A , l) and the storage conditions (temperature, a_w), were included. The Oswin equation was used in the spreadsheet to turn the moisture content value of the product into the corresponding water activity value. The water activity value is necessary to calculate the driving force as difference between the outside water activity and the product water activity.

The values listed in the second column of table 2 report the shelf life predicted for each sample by the prediction model.

To evaluate the influence of the difference between the relative humidity of the headspace and the relative humidity of the product on the shelf life prediction the Microsoft Excel spreadsheet model has been modified applying the linear correlation previously described (Equation 1). This correction allowed to consider the lower value of relative humidity described by equation 1 and the consequent delay of time to reach the critical moisture content, leading to a longer shelf life prediction for all the samples considered. The corrected values of shelf life are reported in table 3 in terms of hours and percentage error.

The application of equation 1 to the spreadsheet model allowed to correct the shelf life for every value of headspace volume/product weight ratio in the range considered during this trial, between 8.7 and 37.5 cm³ g⁻¹.

Figure 4 shows how, in the considered range, to the increase of the ratio headspace volume/product weight corresponds an increase of the percentage error on the shelf life prediction, following a linear relationship. The increase of the errors underlines the importance of the correction to the prediction model.

Table 3: shelf life prediction values.

Sample number	Predicted SL [h]	Headspace volume/Product weight [cm ³ g ⁻¹]	Corrected SL [h]	SL Error [h]	SL Error [%]
1	85	26.1	106	21	19.8
2	63	37.5	83	20	24.1
3	129	15.5	149	20	13.4
4	94	23.1	112	18	16.1
5	170	10.2	192	22	11.5
6	188	8.7	211	23	10.9

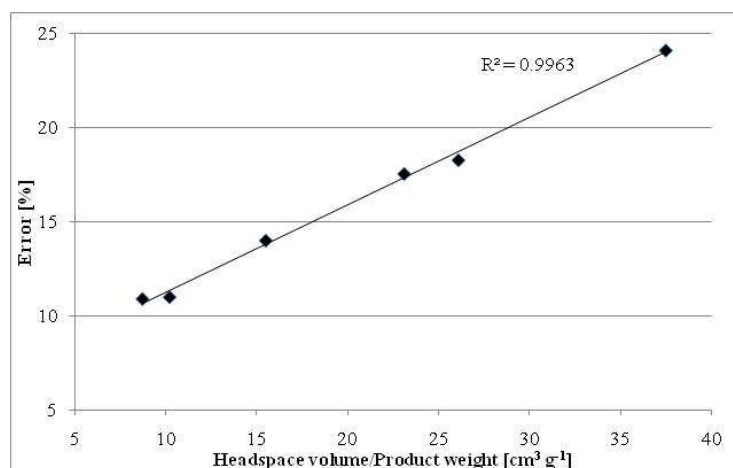


Figure 4: relationship between headspace volume and $\Delta\%$ RH

4. Conclusions and future perspectives

The model system studied in the present work has demonstrated that, in this case, the theoretical assumption generally used in the shelf life modelling, stating the immediate equilibrium between the headspace and the product relative moistures, is not verified. These relative moistures are not immediately in equilibrium but show an increasing difference correlated to the increase of the headspace volume/product weight ratio. This correlation has been studied and it has been described by a linear equation in the considered range.

The application of a shelf life prediction model to the studied system has shown that a correction is needed to avoid an underestimation of the shelf life.

Further studies on other types of moisture sensitive products will be necessary to confirm the results obtained.

The application of this correction will be particularly interesting for the shelf life modelling of moisture depending products characterized by packaging solution with high headspace volumes.

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